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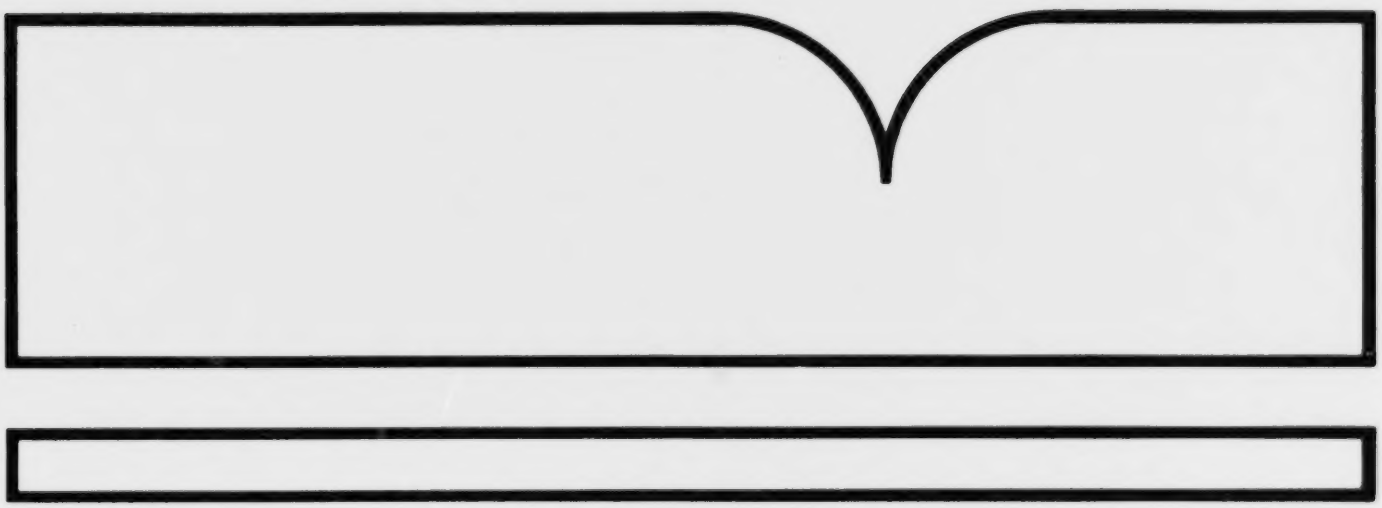
Materials Balance for Benzene
Level I - Preliminary

JRB Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC

9 May 80



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Materials Balance for Benzene

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16. ABSTRACT

A Level I materials balance was performed on benzene. Data are reported for benzene production from petroleum by four processes (catalytic reformation, toluene dealkylation, toluene disproportionation, and isolation from pyrolysis gasoline) and for production from coal during coking. Amounts of benzene consumed for the synthesis of nine direct derivatives (ethylbenzene, cumene, cylcohexane, nitrobenzene, maleic anhydride, mono- and dichlorobenzenes, alkylbenzenes, anthraquinone, and biphenyl) and exports are presented. These uses constitute approximately 93 percent of total benzene usage. Nonconsumptive uses (solvents and inventory changes) are also tabulated. Emissions due to each of the above processes are reported or estimated where possible. In addition, emissions due to indirect production (refinery operation, coke oven operations, oil spills, non-ferrous metals manufacturing, ore mining, wood processing, coal mining, and two phases of the textile industry) are presented. Production of benzene as a component of gasoline and emissions due to gasoline use are estimated. Locations of sites with high densities of benzene producers and users are tabulated: the major "hotspots" are Houston/Galveston, Texas; Corpus Christi, Texas; Beaumont/Port Arthur, Texas; and Puerto Rico. The uncertainty ranges of all numbers used or derived in this report are evaluated and general recommendations are presented. The results of the report are summarized in two figures: the Environmental Flow Diagram for benzene in Appendix A, and the Materials Balance Diagram in the Executive Summary.

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FINAL REPORT

LEVEL I MATERIALS BALANCE

BENZENE

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
SURVEY AND ANALYSIS DIVISION

Task No. 16
Contract No. 68-01-5793
Michael Callahan - Project Officer
Elizabeth F. Bryan - Task Manager

Prepared by:

JRB ASSOCIATES, INC.
8400 Westpark Drive
McLean, Virginia 22102

Project Manager:	Karen Slimak
Task Leader:	Robert L. Hall
Contributing Writers:	Carlos Buitrago Frank Montecalvo Tom Yatsko

Submitted: May 9, 1980

THIS IS A DRAFT REPORT ON A LEVEL I MATERIALS BALANCE ON BENZENE. AS SUCH, IT IS PRESENTED AS A FOCUS OF DISCUSSION AND AS A BASIS FOR FUTURE MATERIALS BALANCE STUDIES; IT IS NOT MEANT TO BE A DEFINITIVE STUDY. THE RESULTS REPORTED WERE BASED ON A 700-HOUR, SEVEN-WEEK ANALYSIS OF A SET OF READILY AVAILABLE LITERATURE SUPPLIED BY EPA. ALTHOUGH SUPPLEMENTARY INFORMATION UNDOUBTEDLY EXISTS, OBTAINING IT WAS OUTSIDE THE SCOPE OF THIS TASK.

MATERIALS BALANCE LEVELS

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below.

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division as a source of data and references involving readily available information. Most Level I MB's are completed within a 3-6 week period; CID literature searches generally require a 2 week period to complete. Thus the total time required for completion of a Level I materials balance ranges from 5-7 weeks.

Level II:

A LEVEL II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A LEVEL III study requires generation of new data through monitoring and other means. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and necessary monitoring. The data generated in this type of study are intended to be statistically valid and have known confidence values. The goal is a study upon which regulations or legal proceedings may be based.

ABSTRACT

A Level I materials balance was performed on benzene. Data are reported for benzene production from petroleum by four processes (catalytic reformation, toluene dealkylation, toluene disproportionation, and isolation from pyrolysis gasoline) and for production from coal during coking. Amounts of benzene consumed for the synthesis of nine direct derivatives (ethylbenzene, cumene, cyclohexane, nitrobenzene, maleic anhydride, mono- and dichlorobenzenes, alkylbenzenes, anthraquinone, and biphenyl) and exports are presented. These uses constitute approximately 93 percent of total benzene usage. Nonconsumptive uses (solvents and inventory changes) are also tabulated. Emissions due to each of the above processes are reported or estimated where possible. In addition, emissions due to indirect production (refinery operation, coke oven operations, oil spills, non-ferrous metals manufacturing, ore mining, wood processing, coal mining, and two phases of the textile industry) are presented. Production of benzene as a component of gasoline and emissions due to gasoline use are estimated. Locations of sites with high densities of benzene producers and users are tabulated: the major "hotspots" are Houston/Galveston, Texas; Corpus Christi, Texas; Beaumont/Port Arthur, Texas; and Puerto Rico. The uncertainty ranges of all numbers used or derived in this report are evaluated when possible and tabulated. Data gaps are evaluated and general recommendations are presented. The results of the report are summarized in two figures: the Environmental Flow Diagram for benzene in Appendix A, and the Materials Balance Diagram in the Executive Summary.

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EXECUTIVE SUMMARY

This Level I materials balance on benzene was performed in response to Task Order No. 16 under Contract No. 68-01-5793 with the Office of Pesticides and Toxic Substances, EPA.

The Materials Balance Summary Diagram for benzene is included at the end of this Executive Summary. It shows only those processes for which data were obtainable. The more comprehensive Environmental Flow Diagram for benzene appears as Appendix A of the report. All data refer to the year 1978 unless otherwise stated.

DIRECT PRODUCTION

Benzene is obtained by the fractionation and enrichment of fossil fuels. It is produced from petroleum by four processes: 1) catalytic reformation of the naphtha petroleum fraction, 2) dealkylation of toluene, 3) disproportionation of toluene, and 4) as a byproduct of ethylene manufacture (isolation from pyrolysis gasoline). Benzene is obtained from coal by extracting it from the light oil formed during coking. This extraction may be done either at the coking plant or after sale of the light oil to refineries. The contribution by each process and the total production of benzene from petroleum are shown below.

Process	kkg Benzene Produced, 1978	% of Total
Catalytic reformation	2,360,000	48
Toluene dealkylation	1,300,000	26
Toluene disproportionation	121,000	2
Pyrolysis gasoline	925,000	19
PETROLEUM SUBTOTAL	4,710,000	95
Extraction of light oil by coking plants	178,000	4
Extraction of light oil by refineries or process unknown	74,000	1
PETROLEUM AND COAL TOTAL	4,960,000	100

Total benzene emissions due to the four production processes (including storage and transport) were estimated to be 2,400-7,900 kkg. These were estimated to be distributed 1,800-7,300 kkg to air, and 630 kkg to water. No estimate of releases to landfills was possible. The above emissions include benzene released during gasoline production by refineries.

Benzene emissions due to benzene-producing coke oven operations could not be estimated.

INDIRECT PRODUCTION

Indirect sources of petroleum were analyzed. Their total estimated benzene emissions were: refinery operations (20,000 kkg to air, 1 kkg to water), coke oven operations (3,000-59,000 kkg to air), oil spills (30 kkg to water), and miscellaneous operations listed on the Materials Balance Summary Diagram.

IMPORTS

225,000 kkg of benzene were imported in 1978. The estimated emissions due to importing were 13 kkg to air and 13 kkg to water.

CONSUMPTIVE USES

The predominant use of benzene is as a starting material for the synthesis of other organic compounds. The nine major direct derivatives of benzene and their contributions to total benzene consumption are listed in Table ES-1.

A summary of the emissions due to synthesis of each product is shown in Table ES-2.

EXPORTS

Exports accounted for 151,000 kkg of benzene in 1978. Estimated emissions due to exportation (dockside loading) were 15 kkg to air, 2 kkg to water, and a negligible amount to land.

Table ES-1 Summary of Consumptive Uses of Benzene

Product	Formed by Reacting Benzene with -	Secondary Products or Uses	kkg Benzene Used, 1978	Percentage of Consumptive Uses
Ethylbenzene	Ethylene	Styrene; Polystyrene	2,890,000	54
Cumene	Propylene	Phenol	1,058,000	20
Cyclohexane	Hydrogen	Cyclohexanone; Nylon 66	811,000	15
Nitrobenzene	Nitric Acid	Aniline	170,000	3
Maleic Anhydride	Oxidant	Chemical Intermediates	161,000	3
Chlorobenzenes	Chlorine	Chemical Intermediates	133,000	2
Alkylbenzenes	10- to 14- Carbon alkyl chlorides	Detergents	132,000	2
Anthraquinone	Phthalic Anhydride	Dyes	23,000	0.4
Biphenyl	Itself (with heat)	PCBs; Dyes	11,000	0.2
			5,389,000	99.6

Table ES-2 Emissions of Benzene Due to Consumptive Uses (1978)

Product Synthesized	Estimated Emissions (kkg) to- Air	Water	Land	Total	Percent of Total [1]
Ethylbenzene	2,600 14,000	720	Uk*	3,300- 15,000	7 - 26
Cumene	Uk	Uk	Uk	380	0.7 - 0.8
Cyclohexane	2,970	30	Uk	3,000	5.3 - 6.7
Nitrobenzene	2,200	Uk	Uk	2,200	3.9 - 4.9
Maleic Anhydride	34,000	Uk	Uk	34,000	60 - 75
Chlorobenzenes	2,060	Uk	Uk	2,060	3.6 - 4.6
Alkylbenzenes	170	Uk	Uk	170	0.3 - 0.4
Anthraquinone	Uk	Uk	Uk	Uk	Uk
Biphenyl	65	0.3	Uk	64	0.1
TOTALS	44,100- 55,500	750	Uk	45,100- 56,800	

*Uk = Unknown

1 The range of values is not a statistical range or set of error limits, but results from the range of total values used.

NONCONSUMPTIVE USES

Approximately 5.1 percent of benzene production was used nonconsumptively in 1977, i.e., benzene was not converted to another compound before use. The categories of nonconsumptive use and the amounts used are:

Use	kkg Benzene Used
Solvent	27,000 (higher estimate)
Inventory Increase	-272,000

Solvent use of benzene has decreased since the 1977 OSHA Emergency Benzene Standard and the 1977 Consumer Products Safety Commission ban on benzene in consumer goods. 1978 emissions due to solvent use were estimated to be 1,450 kkg to air, 1,450 kkg to water, and an unknown amount to land.

The inventory of benzene as of January 1, 1979, was 272,000 kkg less than on January 1, 1978. This decrease in inventory is treated as increased supply when balancing benzene sources with benzene sinks.

BENZENE AS A FUEL CONSTITUENT

The largest single source of benzene emissions is due to its presence as a minor component of gasoline. The production of gasoline by refineries is a major indirect source of benzene, generating an estimated 7×10^6 kkg of benzene in 1979. Emissions due to refining are included under petroleum refining operations above. Other sources of emissions are listed below:

Process	Emissions to air, kkg, 1979
Gasoline storage	4,000
Gasoline transport	3,000
Gasoline vending	7,000
Gasoline combustion	30,000 - 70,000
Sum:	40,000 - 80,000 kkg

The difference between the amount of benzene consumed in gasoline (7×10^6kkg) and total benzene emissions due to fuel use ($4\text{-}8 \times 10^4$kkg) was $6.92\text{-}6.96 \times 10^6$kkg. This value represents the difference: (benzene destroyed by combustion minus benzene generated by combustion). Since the amount generated is not known, this difference is reported as benzene destroyed.

Geographic distribution of benzene emissions due to gasoline use had not yet been analyzed at the time of submission of this revised draft.

DISPOSAL/DESTRUCTION OF END-PRODUCTS

No information was readily available to permit estimation of benzene emissions due to landfilling or incineration of benzene-containing solid residues or of benzene-containing end-products.

LOCATIONS OF MAJOR BENZENE EMISSION SITES

Tabulation of sites and production/consumption volumes at those sites indicated that the top five counties for potential benzene emissions were in Texas: Harris, Galveston and Brazoria Counties (Houston/Galveston area), Nueces County (Corpus Christi), and Jefferson County (Beaumont/Port Arthur). The sixth most likely emission region is Puerto Rico. This tabulation does not include emissions due to the presence of benzene in gasoline.

UNCERTAINTIES AND DATA GAPS

Whenever a basis for evaluation existed, an attempt was made to quantify the uncertainties of estimates. These uncertainties were expressed as a range of values.

The following data gaps were encountered in performing this study: 1) Lack of information on benzene emissions at coke ovens. A literature search and industry inquiries are recommended. 2) Lack of breakdown of petroleum-based benzene emissions by process (catalytic reformation,

toluene disproportionation, etc.). A literature search and possible monitoring of air emissions are recommended. 3) Lack of information on benzene emissions to water. These emissions are generally assumed to be small, but the assumption is important and needs to be confirmed by a literature search and industry inquiries. 4) Lack of information on generation and disposal of benzene-containing solid residues during production and consumptive uses. Industry inquiries are recommended. 5) Lack of information on emissions due to minor consumptive uses: synthesis of anthraquinone and biphenyl. A search of specialized literature is recommended. For instance, dye industry literature may be a source of information on anthraquinone, and literature on PCBs may yield data on biphenyl emissions.

SUMMARY OF EMISSIONS BY CATEGORY

The table below summarizes estimated emissions by major category of production and use.

Category	Estimated kkg Emitted[1] to- Air	Water	Land	Total
Production from Petroleum	1,800-7,300	630	?	2,400-7,900
Production from coal	?	?	?	?
Imports	13	13	?	25
Indirect Production	23,000-79,000	200-11,000	?	23,000-90,000
Consumptive Uses	44,000-56,000	1,000	?	45,000-57,000
Nonconsumptive Uses	1,450	1,450	?	2,900
Component or Gasoline	40,000-80,000	?	?	40,000-80,000
SUMS:	110,000-220,000	3,000-14,000	?	110,000-240,000

1. A range of values is not meant to be a statistical range or set of error limits, but results from differing independent estimates of the emissions.

SUMMARY: MATERIALS BALANCE FOR BENZENE

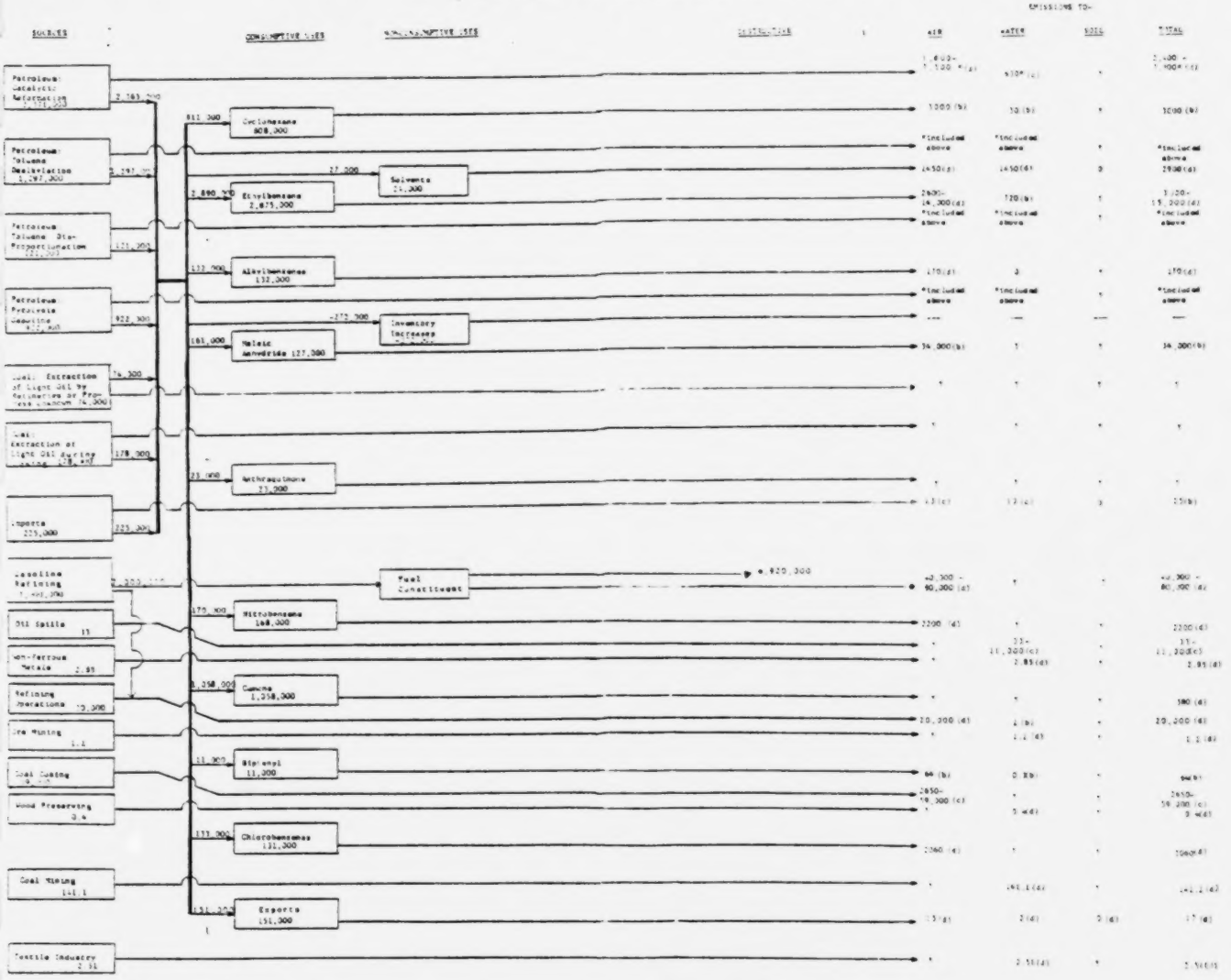
The diagram summarizes the data and estimates available at present for the materials balance for benzene. It shows a breakdown of the categories in the table above into individual processes. Operations for which no data were available were not included. In particular, there are no entries under Carryover to Product and Destruction. These will be important topics for a Level II materials balance on benzene.

The "balance" equation for the materials balance is shown below. It was formulated as follows:

Benzene available	=	Benzene accounted for by uses + losses + storage
Production + Imports	=	Consumptive uses + Exports + Inventory changes + Destruction + Emissions
12,300,000 kkg	=	5,480,000 kkg + (-272,000 kkg) + 6,920,000 + 240,000 kkg
12,300,000 kkg	=	12,400,000 kkg

The apparent imbalance of 100,000 kkg may be explained by the fact that consumptive use amounts were calculated independently from direct production amounts. The imbalance also obscures the fact that 21,000 kkg used as a solvent were unaccounted for as emissions, and thus can be considered as having been "stored". The excess of 121,000 kkg on the "uses" side of the balance represents one percent of the benzene available. We feel this is within the uncertainty range of the respective totals.

EXECUTIVE SUMMARY - MATERIALS BALANCE FOR BENZENE, 1978 (MKG)



(): +/- -- Estimated Uncertainties

(a) = ± a factor of 1 or better
(b) = ± a factor of 2-10
(c) = ± a factor of 10-1000
(d) = no basis for estimation

1.0 INTRODUCTION

This Level I materials balance on benzene was prepared in response to a task order from Survey and Analysis Division, U. S. Environmental Protection Agency. The report is organized according to the processes during which benzene might be emitted to the environment (direct production, consumptive use, etc.). In order to present the large amount of available information most clearly, current (usually 1978) data are presented in tables interspersed in the text of each chapter and five year trends (1979-1975) are presented in tables at the end of the chapter.

In the tables and figures reporting emissions data and estimates, the term "releases to land" was defined as meaning "material applied to the soil," as opposed to material applied to a landfill. A landfill has been interpreted as a form of waste storage rather than as a sink. The rationale was that benzene-containing solids in a landfill would readily lose benzene by leaching or evaporation to yield water or air releases. Therefore, benzene-containing solids applied to a landfill have been apportioned to air and water to reflect long-term reality. On the other hand, actual "releases to land" would include use of pesticides, fertilizers, or other chemicals that would yield benzene due to microbial or photochemical degradation. Such releases would be tabulated as indirect production of benzene.

1.1 PROPERTIES OF BENZENE

Benzene is a clear, flammable liquid with a pungent odor. Its physical properties are summarized below (Weast, 1977-78; Strecher, 1968):

Melting Point	5.5°C
Boiling Point	80.1°C
Density	0.87865 g/cc
Solubility in H_2O	0.70 g/l at 25°C
Temperature at which vapor pressure = 1 Torr	-36.7°C

Benzene's physical properties indicate a compound likely to be emitted to air or to evaporate to air from the surface of a biphasic water mixture. Benzene's density value has been used to convert volumes to kkg. No temperature correction was applied to the density value.

1.2 ENVIRONMENTAL FLOW DIAGRAM FOR BENZENE

Appendix A shows the environmental flow diagram for benzene. This diagram attempts to demonstrate as many as possible of the sources and uses of benzene, as well as potential points of release to the environment. It is not our purpose to complete the diagram--or even to discuss it in detail--in this report. It serves as a guide, however, in formulating the questions to be asked in this and other benzene materials balances.

2.0 DIRECT PRODUCTION OF BENZENE

Benzene is directly produced from two sources: from coal during coke production, and from petroleum by various methods. While coal was the original source of benzene (Kirk-Othmer, 1976), petroleum is the primary source of benzene today. In 1978 according to the U.S. International Trade Commission, 178,000 kkg of benzene were obtained from coal while 4,780,000 kkg were derived from petroleum.

2.1 PRODUCTION FROM PETROLEUM

It has been known for many years that benzene is present in small amounts in crude oil. Recovery of this benzene fraction is uneconomical unless the benzene concentration is increased by some catalytic or thermal reaction. There are four basic methods by which benzene is produced from petroleum: (1) catalytic reformation, (2) dealkylation of toluene, (3) disproportionation of toluene, and (4) from pyrolysis gasoline (Kirk-Othmer, 1976). Some refineries also recover benzene from purchased light oil (coal derived). This benzene is included in total production from coal.

2.1.1 Producers and Locations

Figure 2.1 shows the locations of U.S. plants producing benzene from petroleum. The majority of these are located on the Texas Gulf Coast, specifically the Houston and Corpus Christi areas.

An additional piece of important information on the figure is the type of process used: catalytic reformation, dealkylation of toluene, disproportionation of toluene, or isolation from pyrolysis gasoline. The data are from SRI (1977) and A.D. Little, Inc. (1977). Some plants were listed in the literature as using more than one process without indication of relative capacities. In these cases, plant capacity was assumed to be evenly distributed among the

Locations

Unplotted - Channelview, TX; St. Croix, VI; Penuelas, PR; Guayama, PR; Alliance, LA; Taft, LA

Figure 2.1 Petroleum-Based Benzene Producers, 1978

Company	Location	Estimated Production[1] (kkg) 1979	1978	1977	1976	1975	Production Processes[2] and Use
Allied Chemical	Winnie, TX				8,520	5,680	
Amerada Hess Corp.	St. Croix, Virgin Islands	162,000	146,000	159,000	71,000	47,400	CR
American Petrofina, Inc.	Port Arthur, TX				42,600	28,400	C
(Cosden Oil & Chemical Co.)	Big Spring, TX	144,000	130,000	142,000	128,000	85,300	CR, TD
Ashland Oil, Inc.	Ashland, KY	159,000	144,000	156,000	142,000	95,000	CR, TD, LO
	North Tonawanda, NY	57,200	51,700	56,200	42,600	28,400	CR, LO
Atlantic Richfield Co.	Houston, TX	139,000	126,000	103,000	125,000	83,400	CR, TP
	Wilmington, CA	29,800	27,000	29,300	34,100	22,700	CR
	Channelview, TX	162,000	146,000	78,200			PG
Charter International Oil Co.	Houston, TX	12,400	11,200	12,200	14,200	9,470	CR
Cities Service Co., Inc.	Lake Charles, LA	62,100	56,200	61,100	71,000	47,400	CR
Coastal States Gas Prod. Co.	Corpus Christi, TX	174,000	157,000	171,000	199,000	133,000	25% C, CR, TD
Commonwealth Oil Refining Co. (Commonwealth Petrochemicals)	Penuelas, Puerto Rico	460,000	416,000	452,000	525,000	350,000	PC, CR, TD, PG
Crown Central Petroleum Corp.	Pasadena, TX	57,200	51,700	56,200	65,300	43,600	CR, TD
Dow Chemical Co.	Bay City, MI	74,600	67,500	73,300	85,200	56,900	C, TD, PG, LO
	Freeport, TX	124,000	112,000	122,000	142,000	94,700	C, TD, PG
	Plaquemine, LA	149,000					
Eastman-Kodak Co. (Texas Eastman Div.)	Longview, TX	?	?	?	?	?	
Exxon Corp.	Baton Rouge, LA	174,000	157,000	171,000	185,000	123,000	CR, PG
	Baytown, TX	149,000	135,000	147,000	176,000	117,000	67% C, CR
Getty Oil	El Dorado, KS	32,300	29,200	31,800	37,000	24,600	C, CR
Gulf Oil Corporation	Alliance, LA	167,000	151,000	164,000	199,000	133,000	C, CR, TD
	Philadelphia, PA	92,000	83,200	90,400	93,700	62,500	C, CR, TD
	Port Arthur, TX	186,000	169,000	97,700	108,000	72,000	C, CR, PG
Kerr-McGee Corp. (Southwestern Oil & Ref. Co.)	Corpus Christi, TX	39,800	36,000				
Marathon Oil Co.	Texas City, TX	17,400	15,700	17,100	17,000	11,400	C, CR
Mobil Oil Corp.	Beaumont, TX	149,000	135,000	147,000	170,000	114,000	CR, PG
Monsanto Co.	Chocolate Bayou, TX	211,000	191,000	208,000	213,000	142,000	C, CR, TD, PG
Pennzoil United, Inc. (Atlas Processing)	Shreveport, LA	87,000	78,700	36,600	42,600	28,400	PG
Phillips Petrol. Co.	Sweeny, TX	24,900	22,500	24,400	62,500	41,700	C, CR
	Guayama, Puerto Rico	273,000	247,000	269,000	312,000	208,000	PC, CR, TD
Quintana-Howell	Corpus Christi, TX	224,000	202,000	17,100			CR

Figure 2.1 Producers and Production, 1975-1979[1] (Continued)

Company	Location	Estimated Production[3] (kkg) 1979	1978	1977	1976	1975	Production Processes[2] and Use
Shell Oil Co.	Deer Park, TX	298,000	270,000	220,000	213,000	142,000	C, CR, PG
	Odessa, TX	29,800	27,000	29,300	17,000	11,400	CR, TD
	Wood River, IL	112,000	101,000	110,000	114,000	76,000	CR, LO
Standard Oil Co. of Calif.	El Segundo, CA	57,200	51,700	56,200	65,300	43,600	C, CR
Standard Oil Co. (Ind.)(AMOCO)	Texas City, TX	211,000	191,000	208,000		161,000	C, CR
Standard Oil Co. (Ohio) (B.P. Oil Co.)	Marcus Hook, PA				22,700	15,200	
Sun Oil Co.	Marcus Hook, PA	72,100	65,200	70,800	42,600	28,400	CR, TP
	Corpus Christi, TX	94,500	85,400	92,800	99,400	66,300	C, CR, TD
	Tulsa, OK	59,700	54,000	58,600	68,200	45,500	CR, TP
	Toledo, OH	184,000	166,000	120,000			CR, TD
Tenneco, Inc.	Chalmette, LA	24,900	22,500	24,400	28,400	18,900	CR, LO
Texaco, Inc.	Port Arthur, TX	112,000	101,000	110,000	128,000	85,300	73% C, CR
	Westville, NJ	87,000	78,700	85,500	99,400	66,300	PC, CR
Union Carbide Corp.	Taft, LA	174,000	157,000	171,000	199,000	133,000	C, PG
Union Oil Co. of Calif.	Lemont, IL	42,300	38,200	41,500	54,000	36,000	CR, LO
Union Oil-American Petrofina	Beaumont, TX	54,700	49,500	53,700	54,000	36,000	50% C, TD
Union Pacific Corp. (Champlin Petroleum Co.)	Corpus Christi, TX	24,900	22,500	24,400	28,400	18,900	C, CR
TOTAL USITC PRODUCTION		5,430,000[3]	4,780,000	4,570,000	4,540,000	3,190,000	

1. Sources: A.D. Little, Inc., 1977; SRI, 1977; Versar, 1979; Neufeld et al., 1978.
2. Key: C= captive use, PC= partially captive, CR= catalytic reformation, TD= toluene dealkylation, TP= toluene disproportionation, PG= pyrolysis gasoline, LO= light oil.
3. Derived from plant capacities and USITC production totals as described in Section 2.1.2.
4. Estimated by extrapolating USITC data for the months January through July, 1979.

Table 2.2 Producers and Production, 1975-1979 (Continued)

processes listed. No allocation was made to the process of recovering benzene from light oil unless specifically indicated in the literature.

The final column on this figure indicates if the production was captively used (A.D. Little, Inc., 1977; SRI, 1977).

2.1.2 Amounts Produced

Figure 2.1 lists U.S. producers of benzene from petroleum and the estimated production by each plant. The years 1975-1979 are included. Company names and locations were compiled from information contained in USITC publications, Versar (1979), Neufeld et al. (1978), and SRI (1977).

Estimated production (kkg) for a given plant in a given year was calculated using the following formula: Estimated production = $\frac{A}{B} \times C$, where A = total production of benzene by petroleum refineries for that year as per USITC information, B = total U.S. plant capacity for that year as per SRI information minus the capacity of plants not listed by USITC as having produced benzene that year, and C = the capacity of the individual plant named (from SRI). Since USITC production is in gallons, a conversion factor of 3.33×10^{-3} kkg = 1 gal has been applied. The other bases for calculation of production figures were: (1) It was assumed that an individual plant's production was proportional to its capacity. (2) Estimates for 1979 were based on USITC data from January - July which were extrapolated to cover the whole year. (3) Plant capacities for 1975-1976 were assumed to be equal to the plant capacities for 1976 as listed in Versar (1979). (4) Plant capacities for 1977-1979 were assumed to be equal to the plant capacities indicated in SRI (1977).

2.1.3 Production by Catalytic Reformation

Of the four methods of producing benzene from petroleum, catalytic reformation is the most commonly used. Of the 43 refineries believed to have been producing in 1978 and for which we also had data on production methods, 37 were reported to have the capacity to produce

benzene by catalytic reformation (See Figure 2.1). The aromatics fraction of petroleum is enriched by the process, which basically converts non-aromatics to aromatics (including benzene) with such reactions as dehydrogenation, isomerization, cyclization, dealkylation, and combinations thereof. The reaction conditions and the catalyst determine which reactions predominate and these reactions' kinetics. Benzene is extracted from the aromatic-rich reformate in a subsequent separation process.

2.1.3.1 Amounts Produced by Catalytic Reformation

Total capacity for benzene production by petroleum refineries was estimated to have been 7,080,000 kkg during 1978. Of this amount 3,500,000 kkg were estimated to be capacity available to the catalytic reformation process (SRI, 1977; Neufeld et al., 1978). Based on a total petroleum-derived benzene production (as opposed to capacity) of 4,780,000 kkg (USITC), 2,360,000 kkg were attributed to production by catalytic reformation. Assuming production was proportional to capacity, for 1978:

$$\text{Production (kkg) by catalytic reformation} = (\text{total production, kkg}) \times \frac{(\text{capacity of catalytic reformation plants})}{(\text{total 1978 benzene capacity})} .$$

Information on plants having catalytic reformation capacity is presented in Figure 2.1.

2.1.3.2 Emissions Due to Catalytic Reformation

Possible sources of emission during catalytic reformation are listed below. These are based on the method called Platforming, a process flow chart of which is presented in Appendix B.

1) Catalyst regeneration by controlled combustion to remove coke.
2) Separator gas.

One method of extracting benzene from the aromatic-rich reformate is the Shell-UOP Sulfolane extraction process. Possible sources of

emissions from this method are listed below. A process flow chart is presented in Appendix B.

1) Raffinate wash water
2) Raffinate

It has been estimated that less than 1% of the benzene produced was lost through reforming operations (Walker, 1976). Thus, a maximum emission factor would be 1×10^{-2} kkg/kkg benzene produced by catalytic reformation. Application of this emission factor to benzene production by this method yielded: (2,360,000 kkg) (1×10^{-2} kkg/kkg) = 20,000 kkg benzene released during production by catalytic reformation of petroleum. This is a maximum value.

No factors for emissions specifically to air, water or land by the catalytic reformation process were found in the literature, thus no emissions to these compartments could be calculated. See also Section 2.1.7.

2.1.4 Production by Dealkylation of Toluene

A second method of benzene production from petroleum is by dealkylation of toluene. Here the petroleum has already been refined to produce toluene, thus raw material costs make benzene produced by this method more expensive than from other sources (Kirk-Othmer, 1976). Dealkylation performed in the presence of hydrogen is known as hydrodealkylation. Toluene hydrodealkylation is performed by a catalytic or thermal process. These processes are equally split in terms of frequency of use, and are very similar to each other. In both processes, toluene is heated and then charged to a reactor in the presence of excess hydrogen. Toluene reacts with the hydrogen to produce benzene and methane gas. The reaction product is separated, stabilized, and distilled to recover benzene. The only difference in the two processes is that the toluene is heated to a higher temperature in the thermal process, and the reaction occurs in the presence of a catalyst with the catalytic process (Kirk-Othmer, 1976).

A newer method of dealkylation, steam dealkylation, reacts toluene with steam to produce benzene, carbon monoxide, carbon dioxide and hydrogen. The advantage is that hydrogen is produced rather than consumed (Kirk-Othmer, 1976).

Of the 43 refineries believed to have been producing benzene in 1978 and for whom we have data on production methods, 15 were reported to have the capacity to produce benzene by toluene dealkylation. (See Figure 2.1.)

2.1.4.1 Amounts Produced by Toluene Dealkylation

Estimated capacity for benzene production by toluene dealkylation was 1,920,000 kkg for 1978 (SRI, 1977; Neufeld et al., 1978). The actual production is estimated to have been 1,300,000 kkg based on USITC data, and calculated using the formula presented in Section 2.1.3.1 above.

Information on plants having toluene dealkylation capacity is presented in Figure 2.1.

2.1.4.2 Emissions Due to Toluene Dealkylation

Possible sources of emission during toluene dealkylation are:

1) Separation of reaction product (benzene, methane)
2) Distillation
3) Regeneration of catalyst (catalytic method only)
4) Separation of benzene from CO, CO_2, + H_2 (steam dealkylation)

No factors for emissions specifically to air, water or land by the toluene dealkylation process were found in the literature, thus no emissions to these media could be calculated. Total emissions due to petroleum-based production are discussed in Section 2.1.7.

2.1.5 Production by Toluene Disproportionation

Toluene disproportionation, also called transalkylation, is the least used of the four methods of producing benzene from petroleum. As with dealkylation, petroleum has already been refined to produce the toluene feedstock (Kirk-Othmer, 1976). Since xylene is simultaneously produced with benzene in this process, the xylene may contain benzene as a contaminant.

One method for toluene disproportionation is the Tatoray Process. An industrial process flow chart for this process is described in Appendix B.

Of the 43 refineries believed to have been producing benzene in 1978 and for which we also had data on production methods, only 3 had the capacity to produce benzene by toluene disproportionation. (See Figure 2.1.)

2.1.5.1 Amounts Produced by Toluene Disproportionation

Estimated capacity for benzene production by toluene disproportionation was 180,000 kkg for 1978 (SRI, 1977; Neufeld, et al., 1978). The actual production was estimated to have been 121,000 kkg as calculated from USITC data and capacity information as described in Section 2.1.3.1.

Information on plants having toluene disproportionation capacity is presented in Figure 2.1.

2.1.5.2 Emissions Attributable to Toluene Disproportionation

Possible sources of emissions due to the Tatoray process presented in Appendix B were:

1) Regeneration/disposal of catalyst
2) Separation process

No factors for emissions specifically to air, water or land by the toluene disproportionation process were found in the literature; no

specific emissions were estimated. Total emissions due to petroleum-based production are discussed in Section 2.1.7.

2.1.6 Production from Pyrolysis Gasoline

In this production method, heavy naphthas or gas oils are steam cracked to produce ethylene and a liquid by-product high in unsaturated aliphatic and aromatic hydrocarbons called dripolene or pyrolysis gasoline. Benzene, toluene, and xylene may be removed from the pyrolysis gasoline by extractive distillation (Kirk-Othmer, 1976). Industrial process flow charts for two extraction processes (Pyrotol and IFP) are presented in Appendix B.

Of the 43 refineries believed to have been producing benzene in 1978 and for whom we also had data on production methods, 11 were reported to have the capacity to produce benzene from pyrolysis gasoline.

2.1.6.1 Amounts Produced from Pyrolysis Gasoline

Estimated capacity for benzene production from pyrolysis gasoline was 1,320,000 kkg for 1978 (SRI, 1977; Neufeld et al., 1978). The actual production was estimated to have been 925,000 kkg based on USITC data and capacity information. The estimation method is described in Section 2.1.3.1.

Information on plants having capacity for production from pyrolysis gasoline is presented in Figure 2.1.

2.1.6.2 Emissions Due to Production from Pyrolysis Gasoline

Possible sources of emissions are:

1) Catalyst regeneration/disposal (IFP process) (gum removal and coke burnoff)
2) Distillation process
3) Separation of benzene from toluene and xylene

4) Pyrotol process steps
   a) gum removal
   b) desulfurization
   c) hydrodealkylation of toluene (see above)
   d) removal of light gases in stabilizer
   e) clay treatment to remove contaminants from stabilized product
   f) distillation

No factors for emissions specifically to air, water or land by the pyrolysis gasoline process were found in the literature; thus, no emissions could be estimated to environmental compartments. Total emissions due to petroleum-based production are discussed in Section 2.1.7.

2.1.7 General Emissions Due to Petroleum-Derived Benzene Production

With the exception of catalytic reformation, no emission factors for the various individual processes by which petroleum-derived benzene may be produced were found in the literature.

Table 2.1 presents two emission factors--one for releases to air and one for releases to water--which may be applied to petroleum-derived benzene production generally (as opposed to production by a specific process).

Applying these factors to the 1978 petroleum-derived benzene production yields approximately 85 kkg benzene emitted to air and 610 kkg benzene emitted to water.

The emission factor for releases to air was based on a Union Carbide estimate for a plant utilizing a crude olefins byproduct stream and is therefore not necessarily representative of other producers. The emission factor for releases to water was based on an average figure for benzene loss to the environment as reported in an industrial questionnaire. The actual values reported in the questionnaire ranged from 0.0006% ti 0.44%. Taking a simple average was probably not valid. Also this emission factor required the assumption that 6% of this loss was to water. No basis for this 6% value was given.

Table 2.1 General Benzene Emission Factors for Benzene Production from Petroleum

Source	Factor	Remarks
--	Releases to Air	--
Based on PEDCo, 1977	1.8×10^{-5} kkg/kkg produced	Based on a Union Carbide estimate of 0.035 lb/ton produced and metric conversion factor 454×10^{-6} kkg/lb and 0.907 kkg/ton. This estimate assumed an aromatics plant utilizing a crude olefins byproduct stream.
--	Releases to Water	--
Based on Versar, 1977	1.3×10^{-4} kkg/kkg produced	(X) x (0.22%) x (6%) Where (X) = annual benzene production, (0.22%) = average annual production lost to the environment (derived from an industrial questionnaire), (6%) = amount of above allocated to water.

The relative sizes of the two emission estimates are also inconsistent with previous results and engineering judgements. The value for emissions to water was greater than that to air. Nothing in the literature indicates that water plays an important part in benzene production. Benzene is volatile and one would expect greater emissions to air. Looking at refinery emissions in general (Section 3.1), emissions to air were considerably greater than emissions to water. This inconsistency may be resolved by more detailed analysis of the primary data in a Level II study.

In estimating the uncertainty of the estimate of emissions to air during benzene production, the main consideration was the validity of extrapolating the Union Carbide single-plant estimate to the entire benzene-from-petroleum industry. While a quantitative estimate of the uncertainty range was not possible, it is suggested that extreme caution be exercised when basing conclusions on the air emissions estimated by this method.

In estimating the uncertainty of the emissions to water during benzene production, two factors were taken into account: (1) the 730-fold range for industrial estimates of percentage of benzene lost to the environment, and (2) the allocation to water of 6% of total losses. Based on these two factors, an uncertainty of $\pm$ a factor of 1,000 was assigned to the estimate of benzene emissions to water.

2.1.8 Emissions Due to Transportation, Loading and Storage Associated with Production of Benzene from Petroleum

2.1.8.1 Sources of Emissions During Storage

Benzene is typically stored in a floating roof storage tank of which there are three types: pan, pontoon, and double-deck floating roof.

With the pan type, extreme tilting may cause the roof to buckle or sink causing a high loss of benzene vapor to the atmosphere. If the roof is in direct contact with the liquid, heating caused by the sun shining on the roof may cause the liquid to boil resulting in an

emission to the air from around the roof's perimeter. The pontoon type and double-deck type were designed to overcome these problems.

All tanks lose vapors at gauging hatches, sample hatches and relief vents unless these points are designed and maintained for proper closure. Also, liquid surface may be exposed to the atmosphere resulting in emissions if the seal between the roof and vessel is improperly fitted. (PEDCo, 1977.)

Benzene loss due to storage can be characterized in two ways, storage standing loss and storage withdrawal loss.

The storage standing loss is caused by the factors mentioned above and increases with the length of storage time.

The act of withdrawing benzene from the tank increases the amount lost, usually from the evaporation of benzene retained on the sides of the tank as the roof sinks (PEDCo, 1977).

Emission factors for these losses are presented in Table 2.2. The first column lists the source of the factor; the second column lists the factor; and the "remarks" column describes how the factor was derived either directly in the reference or from reference data, the assumptions to be used when applying the factor, and other information.

Applying the first two factors listed in the table to the total 1978 benzene consumption of 5,389,000 kkg as reported in Section 5.1, and using a conversion factor of 3.33×10^{-3} kkg/gallon, it was estimated that 100 kkg of benzene were lost due to standing storage, and 5.4 kkg were lost due to storage withdrawal. The sum of these was 105 kkg lost to air due to storage.

Applying the SRI emission factor to total benzene consumption in 1978, assuming uncontrolled storage, and assuming that all benzene consumed has been stored, 4,900 kkg of benzene were lost due to storage.

In the absence of information that would permit choosing between these two disparate emission estimates, the emissions to air due to storage are presented as 105-4,900 kkg.

Table 2.2 Benzene Emission Factors for Storage

Source	Factors	Remarks
Based on PEDCo, 1977	8×10^{-8} kkg/gal benzene consumed Storage standing loss	$\frac{(X)\ (30)\ (4.6 \times 10^{-3})}{(0.75)\ (2.3 \times 10^{6})}$ = kkg benzene emitted Where X = benzene consumption in gallons 30 = retention time in days (assumed) 4.6×10^{-3} = tank emission factor kkg/tank/day 0.75 = tanks are 75% full (assumed) 2.3×10^{6} = size average storage tank in gallons
PEDCo, 1977	3.4×10^{-9} kkg/gal benzene consumed Storage withdrawal loss	$\frac{(X)\ (7.4 \times 10^{-6})}{2.2 \times 10^{3}}$ = kkg benzene emitted Where X = benzene consumption in gallons 7.4×10^{-6} = withdrawal loss in lbs/gal 2.2×10^{3} = lbs/kkg
SRI, 1978	3.0×10^{-6} kkg/gal benzene stored Uncontrolled Storage 0.3×10^{-6} kkg/gal Internal floating roof, vapor recovery	SRI included these estimates when calculating emissions from certain refineries as presented in Figure 3.1.

2.1.8.2 Sources of Emissions During Loading

Benzene is transported by rail tank cars, tank trucks, barges on inland waterways, and pipelines. Before benzene is transported, it is first collected and temporarily stored in a tank called a rundown tank, where it is inspected for product quality. Then it is transferred to two sets of shipping tanks, one for railcar and truck loading and the other for barge loading. The railcar and truck loading tank also issues to the pipelines. Benzene losses from these tanks may be characterized as standing losses (caused by evaporation around perimeter roof seals) and withdrawal losses (occurring as the tank is emptied). Emission factors for these processes are presented in Table 2.3. (Dunavent, 1978.)

Loading losses are produced as liquid benzene is pumped into the carrier and vapors present (either from previous loads or currently generated) are displaced. Emission factors for railcars, trucks, and barges are also presented in Table 2.3. (Dunavent, 1978.)

Before applying these emission factors, it was necessary to determine the amount of benzene that was not captively used in production of other chemicals. Of a total production capacity of $2{,}125 \times 10^6$ gallons for companies actually producing benzene in 1978, 987×10^6 gallons are allocated to captive use, thus, $1{,}138 \times 10^6$ gallons may be allocated to non-captive production. These figures are based on data from USITC, A.D. Little (1977), and SRI (1977). It was assumed that any refinery listed as "partly captive" without further breakdown is actually 50% captive. Applying these data to total production by refineries (including extraction of light oil), as shown below, the total benzene production not captively used was determined:

$$\frac{1{,}138}{2{,}125} \times 4{,}780{,}000 \text{ kkg} = 2{,}560{,}000 \text{ kkg benzene not captively used}$$

Applying the emission factor to this number with a conversion factor of 3.33×10^{-3} kkg/gallon, and assuming that all the benzene passes through the rundown tank, and 50% of the benzene is loaded on railcars

Table 2.3 Benzene Emission Factors for Loading Operations

Source	Factor	Remarks
Based on Dunavent, 1978	Rundown Tank:	Converted from estimated emissions for a 40 x 10^6 gal capacity petroleum-derived benzene plant working at capacity.
	Standing: 6.4 x 10^{-8} kkg/gal	$\frac{5,600 \text{ lbs emitted}}{2.2 \times 10^3 \text{ lbs/kkg}} \div 40 \times 10^6$ gal = emissions benzene/gal produced
	Withdrawal: 5.8 x 10^{-8} kkg/gal	$\frac{5,100 \text{ lbs}}{2.2 \times 10^3 \text{ lbs/kkg}} \div 40 \times 10^6$ gal = emissions benzene/gal produced
Based on Dunavent, 1978	Rail car/Truck loading tank	Converted from estimated emissions for a 40 x 10^6 gal capacity petroleum-derived benzene plant working at capacity; 28 x 10^6 gal of this are handled through railcar/truck loading tanks (14 x 10^6 gal of this later placed in pipeline); the remaining 12 x 10^6 gal are handled through barge loading tanks.
	Standing: 1.7 x 10^{-7} kkg/gal loaded	$\frac{10,200 \text{ lbs}}{2.2 \times 10^3 \text{ lbs/kkg}} \div 28 \times 10^6$ gals loaded rail/truck
	Withdrawal: 3.6 x 10^{-8} kkg/gal loaded	$\frac{2,200}{2.2 \times 10^3} \div 28 \times 10^6$
	Barge loading tank	
	Standing: 4.6 x 10^{-7} kkg/gal loaded	$\frac{12,100}{2.2 \times 10^3} \div 12 \times 10^6$
	Withdrawal: 3.0 x 10^{-8} kkg/gal loaded	$\frac{800}{2.2 \times 10^3} \div 12 \times 10^6$
Based on Dunavent, 1978	Loading Losses	Assume 10 x 10^6 gals loaded in railcar and 4 x 10^6 gals loaded on truck tankers; 12 x 10^6 gals loaded on barges.
	Railcar: 1.3 x 10^{-6} kkg/gal loaded	$\frac{28,900}{2.2 \times 10^3} \div 10 \times 10^6$ gals
	Truck: 1.3 x 10^{-6} kkg/gal loaded	$\frac{11,600}{2.2 \times 10^3} \div 4 \times 10^6$ gals
	Barge: 1.1 x 10^{-6} kkg/gal loaded	$\frac{28,900}{2.2 \times 10^3} \div 12 \times 10^6$ gals

or trucks, and 50% is loaded on barges, the following emissions may be determined:

From rundown tanks -		
	standing:	49 kkg
	withdrawal:	45 kkg
From railcar/truck loading tanks -		
	standing:	64 kkg
	withdrawal:	14 kkg
From barge loading tanks -		
	standing:	176 kkg
	withdrawal:	12 kkg
From loading losses to:		
	railcars/trucks:	500 kkg
	barges:	423 kkg
TOTAL BENZENE EMISSIONS DUE TO LOADING OPERATIONS:		1,300 kkg

No independent criteria were available with which to judge the uncertainty ranges of these estimates.

2.1.8.3 Emissions During Transit

Emission factors for emissions during transit are summarized in Table 2.4. The first factor listed assumes equal distribution between rail/truck and marine transit, and does not include emissions due to loading and unloading. Applying this factor to the amount of benzene not captively used in 1978 yields 270 kkg of benzene lost due to transit.

The SRI factors listed are for specific modes of conveyance. It is not known whether these factors include emissions due to loading/unloading. Applying these factors to the amount of benzene not captively used and assuming 50% is transported by rail-truck and 50% by barge, yields:

losses from transit by rail-truck:	690 kkg
losses from transit by barge:	290 kkg
TOTAL TRANSIT LOSS:	980 kkg

Table 2.4 Benzene Emission Factors for Transportation

Source	Factors	Remarks
Based on PEDCo, 1977	3.6×10^{-7} kkg/gal For Transit	$\frac{(0.78)\ (X)}{(2.2 \times 10^3)\ (1{,}000)}$ = kkg benzene emitted Where (0.78) = assumed transit loss lbs/wk/10^3 gals Where (2.2×10^3) = lbs/kkg (1,000) = gals/10^3 gals Where (X) = gallons transported Assume transport for 1 week Here it also is assumed that half the benzene is transported by truck or tank car, half by marine operations. Emissions due to loading/unloading are not included in this factor.
SRI, 1978	0.76×10^{-6} kkg/gal inland barge 1.8×10^{-6} kkg/gal tank truck 1.8×10^{-6} kkg/gal rail car All above uncontrolled	It is unknown if these factors include losses from loading/unloading

No independent criteria were available with which to judge the uncertainty ranges of these estimates.

2.1.8.4 Total Emissions Due to Transportation, Loading, and Storage

The sum of estimated emissions for transport, loading, and storage operations for petroleum-derived benzene was:

105-4,900 kkg (storage) + 1,300 kkg (loading) + 980 kkg (transport)

= 2,400-7,200 kkg benzene emitted.

Due to the nature of the losses (evaporation), this total emission was judged to be a release to air. The range of values presented is neither a statistical range nor a set of error limits. It was not possible to estimate the uncertainties of the emission factors used; therefore, the uncertainties of the emissions estimates could not be determined.

2.2 BENZENE PRODUCTION FROM COAL

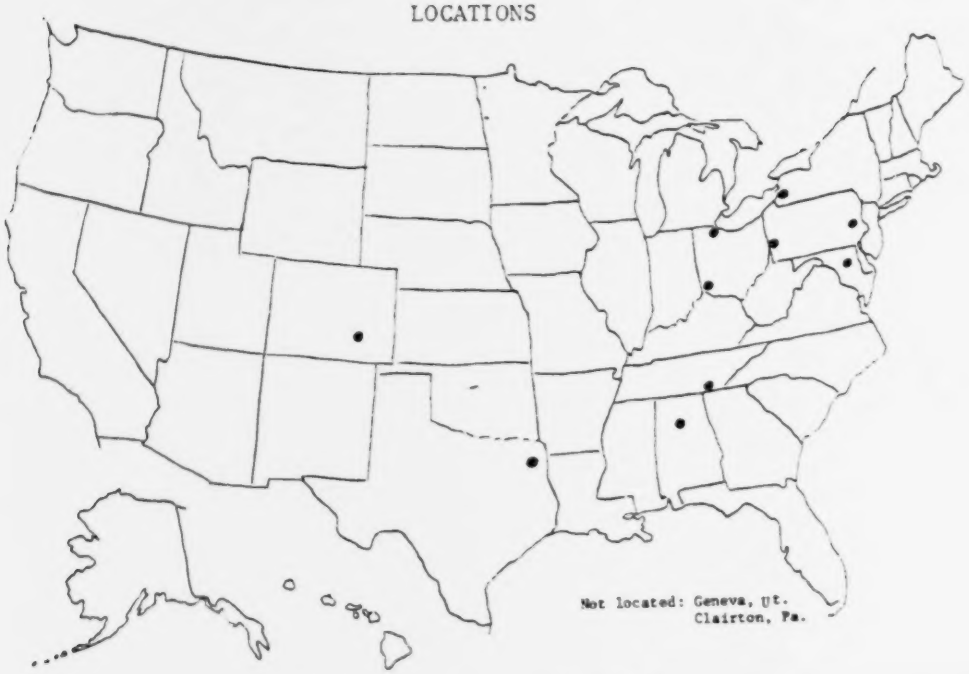
2.2.1 Summary

Figure 2.2 shows the production and location of producers of benzene from coal. Company names and locations were compiled from information contained in Versar (1979) and Neufeld et al. (1978). Estimated production (kkg) for the years 1975-1979 was calculated using the following formula:

$$\frac{A}{B} \times C = \text{Estimated production}$$

where A = total U.S. production of coal-derived benzene for the year under consideration as per USITC information, B = total U.S. plant capacity for that year, and C = the capacity of the individual plant named (capacity information as per Versar, 1979; SRI, 1977; and Neufeld et al., 1978). It was assumed that all plants with listed capacity were producing benzene in proportion to that capacity. Since USITC production is listed in 1,000 gallons, a conversion factor of

LOCATIONS



PRODUCTION OF BENZENE FROM COAL

Coal-derived Benzene Producers[1]		Estimated Production (kkg)[2]					Plant Capacities Used in Estimations: 10^6 gal[3]		
Company	Location	1979	1978	1977	1976	1975	1978-79	1977	1975-76
Armco Steel Corp.	Middletown, OH	6,500	5,700	7,300	6,400	6,900	3	3	3
Bethlehem Steel Corp.	Bethlehem, PA	8,700	7,700	9,800	8,600	9,200	4	4	4
	Lackawanna, NY	0	0	0	17,000	18,000	0	0	8
	Sparrows Point, MD	33,000	29,000	37,000	32,000	35,000	15	15	15
Mead Corporation	Chattanooga, TN	0	0	0	0	0	0	0	0
	Woodward, AL	4,400	3,800	4,900	0	0	2	2	0
C.F. & I. Steel Corp.	Pueblo, CO	6,500	5,700	7,300	6,400	6,900	3	3	3
Interlake, Inc.	Toledo, OH	2,200	1,900	2,400	2,100	2,300	1	1	1
Jones & Laughlin Steel Corp. (LTV Corp)	Aliquippa, PA	22,000	19,000	24,000	21,000	23,000	10	10	10
Northwest Industries, Inc. (Lone Star Steel Corp)	Lone Star, TX	2,200	1,900	2,400	2,100	2,300	1	1	1
U. S. Steel Corp.	Clairton, PA	109,000	96,000	110,000	96,000	104,000	50	45	45
	Geneva, UT	8,705	7,700	9,800	8,600	9,200	4	4	4
Actual Total Production by U. S. Coke Oven Operators (kkg) (USITC)		202,397	178,062	215,021	201,169	216,617	93	88	94

1. Sources: Versar, 1979; Neufeld et al., 1978.

2. Estimates for individual plants based on capacity estimates. See section 2.2.2.

3. Sources: Versar, 1979; SRI, 1977; Neufeld et al.,,1978.

Figure 2.2 Coal-Derived Benzene Producers

3.33×10^{-3} kkg = 1 gallon has been applied. Estimates for 1979 were based on USITC data from January-July which were extrapolated to cover the whole year. Plant capacities for 1975-1976 are assumed to be equal to capacity for 1976 as listed in Versar (1979). Plant capacities for 1977-1979 are assumed to be equal to the 1977 plant capacities indicated in SRI (1977) and Neufeld et al. (1978).

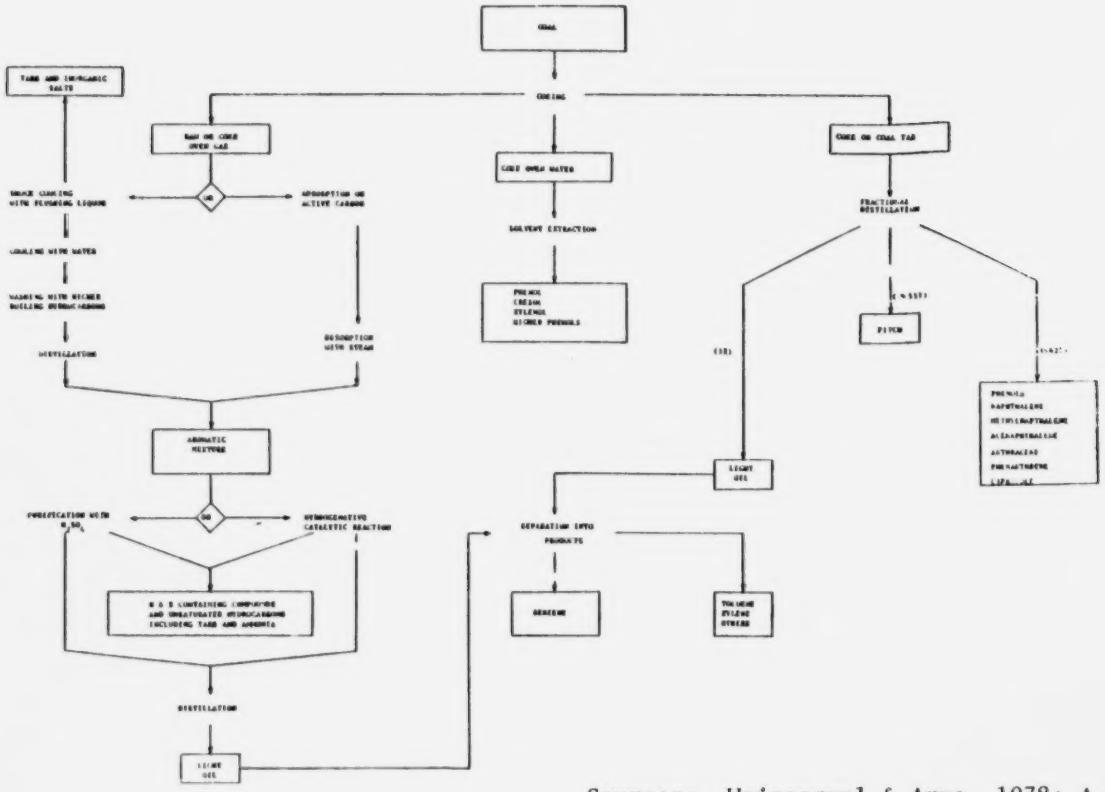
2.2.2 Benzene Production from Coal - the Process

Benzene is produced as a byproduct of the carbonization of coal to coke. Coal is heated in a byproduct oven in the absence of air, driving off the volatile gases. These hot gases are collected overhead and shocked-cooled with a flushing liquor, which results in the removal of a large portion of the tars and inorganic salts. The gases are further processed to remove additional tars and ammonia. The gas is cooled once more with water, then scrubbed with a high-boiling absorbant petroleum oil in a tall column. The wash oil removes the light oil containing benzene, toluene, xylene, etc., from the gas, and the wash oil/light oil mixture is separated by steam distillation. The crude light oil consists of 55-70% by volume benzene. (A.D. Little, 1977.) The yield of light oil from coke ovens producing blast furnace coke is 3-4 gals/ton coal carbonized (PEDCo, 1977).

Another source of light oil is coal tar. Coal tar may be fractionally distilled to yield a light oil fraction which is usually combined with the light oil from coal gas before further refining for benzene (PEDCo, 1977). Light oil produced is either refined on site or is sold. Several petroleum refiners refine this coal-derived light oil (SRI, 1977; A.D. Little, 1977).

The light oil is refined by various processes resulting in its separation into benzene, toluene, xylene, and residue fractions. Benzene recovered from coke oven gas amounts to typically 1.85 gals/ton coal carbonized (PEDCo, 1977).

A schematic diagram summarizing benzene production from coal is presented in Figure 2.3. This diagram is based upon information presented in Weissermel et al. (1978) and A.D. Little (1977).



Sources: Weissermal & Arpe, 1978; A.D. Little, 1977

Figure 2.1 Flow Diagram for Coal Processing

2.2.2.1 Amount Produced

In 1978, 178,000 kkg of coal-derived benzene were produced according to the USITC. This was 4% of total benzene production.

2.2.2.2 Emission During Coal-derived Benzene Production

Possible sources of emissions during production of benzene from coal are:

1) Flushing liquor shock cooling (removing tars and inorganic salts)
2) Tar and ammonia removal
3) Second water cooling
4) Scrubbing process (washing with higher-boiling oils)
5) Wash oil/light oil separation and steam distillation
6) Light oil separation

No emission factors specifically related to the production of benzene from coal were found in the literature, thus no emissions attributable to this process were calculated. Emission factors for the coal coking process in general were found, and are presented in the section related to indirect production of benzene, Section 3.3. No emission factors for transportation, loading and storage of coal-derived benzene were found in the literature; therefore, no emissions were calculated.

2.3 SUMMARY

The total amount of benzene produced in the U.S. according to the USITC for 1978 was 4,960,000 kkg, of which 4,710,000 kkg were petroleum-derived and 252,000 kkg were coal-derived. The petroleum-derived portion may be further broken down by the following estimates: 2,360,000 kkg from catalytic reformation; 1,300,000 kkg from toluene dealkylation; 121,000 kkg from toluene disproportionation; and 925,000 from pyrolysis gasoline. Coal-derived benzene was produced as follows: 178,000 kkg by coke-oven operators, and 74,000 kkg by extraction of purchased light oil at refineries and by unnamed methods. Total

estimated emissions from petroleum-derived benzene production (exclusive of storage and transportation) were 85 kkg to air and 610 kkg to water. Emissions to land were unknown. Maximum total emissions due to catalytic reformation were estimated to be 20,000 kkg. Losses to air from petroleum-derived benzene loading, storage and transportation ranged from 2,400 to 7,200 kkg. Emissions specifically attributable to coal-derived benzene were unknown, but would be included in any emissions from coke ovens (See Section 3.2).

3.0 INDIRECT PRODUCTION OF BENZENE

3.1 INDIRECT PRODUCTION OF BENZENE FROM REFINING OPERATIONS

Since crude oil contains an average of 0.2 percent benzene (Walker, 1976), it can be expected that petroleum refining operations in general would be a source of benzene emissions. The literature revealed several emission factors for benzene to air and to water. These are presented in Table 3.1.

The Mara and Lee (1978) factors were based on average hydrocarbon emissions and percent of the total hydrocarbon emissions attributed to benzene. It was estimated by Mara and Lee that emissions from refineries with catalytic reforming capacity would be double those of other refineries. The extra emissions result from storage losses for gasoline (approximately 50 percent), which is apparently produced from catalytic reformate exclusively. Other sources of emissions are leaks and stacks. Using a list of petroleum refineries and their capacities, Mara and Lee applied these factors along with metric conversion factors to determine total benzene emissions to air. Emissions due to storage and loading of pure benzene were estimated and added for those refineries producing pure benzene not captively used. Controlled emissions were assumed only for those refineries where information on emission control technology was available. Full-capacity production was assumed. These emissions were totaled state by state and appear on the map presented in Figure 3.1. Total U.S. benzene emissions to air from petroleum refineries operating at 1977 capacity were estimated by this method to be 20,000 kkg.

The PEDCo emission factors, which were not applied, were considerably less than those of Mara and Lee. The largest PEDCo factor, that for uncontrolled refineries, was one half that of the smallest Mara and Lee factor.

One factor for emissions to water from petroleum refining was calculated based on data presented in Versar (1977). That source examined

Table 3.1 Benzene Release Factors - Petroleum Refineries

Source	Factor	Remarks
		Releases to Air from Petroleum Refineries
Mara and Lee (1978)	*4.6 lbs Benzene / 1,000 bbl crude refined	Calculated from $\frac{920 \text{ lbs}}{1{,}000 \text{ bbl}}$ (0.5%) where 920 lbs = estimated hydrocarbon releases per 1,000 bbl and (0.5%) = estimated % of hydrocarbons attributed to benzene. Applies to refineries without catalytic reformation benzene production
	*9.2 lbs Benzene / 1,000 bbl crude refined	Calculated from $\frac{920 \text{ lbs}}{1{,}000 \text{ bbl}}$ (1.0%) where 1.0% = estimated % of hydrocarbons attributed to benzene. Applies to refineries with catalytic reformation benzene production
PEDCo (1977)	0.415 lbs/1,000 bbl	For controlled refineries
	2.27 lbs/1,000 bbl	For uncontrolled refineries
	0.759 lbs/1,000 bbl	Weighted industry average
		Releases to Water from Petroleum Refineries
Based on Versar (1977)	1.64×10^{-10} kkg/bbl	(1 µg/l)(43.36 gals water used per bbl)(3.785 l/gal) x (10^{-12} kkg/µg) From Effluent Guidelines Division screening sampling data, benzene was detected in 1 of 6 refineries and the concentration was 0.01 ppm, therefore average concentration is 1 ug/l.

*Factor used in Figure 3.1

EPA Effluent Guidelines Division screening sampling data for six refineries and found that one refinery had a benzene concentration of 6 µg/l in its effluent while the other five had none. The source took the average concentration (1 µg/l), the average amount of water used per barrel of crude refined, information on the number of refineries discharging directly, and metric conversion factors and applied these to the number of barrels refined to estimate the amount of benzene emitted. Using this same method, we calculated the factor presented in Table 3.1. The reliability of this factor is low due to the small amount of data upon which it was based. Since it was the only emission factor available for benzene emissions to water from petroleum refining, it was applied to the petroleum refining capacities listed in Mara and Lee in order to have an order of magnitude estimate of such emissions in 1978. We assumed capacity production and direct discharge of effluent from all refineries. The results of our calculations appear on the map in Figure 3.1 as state totals. Based on the assumptions stated above, total U.S. generated benzene emissions to water from petroleum refineries was approximately 1 kkg in 1978.

Some possible sources of benzene emissions from petroleum refineries indicated by PEDCo (1977) are:

1. Process emissions from light and heavy naphtha streams from the crude unit, fluid catalytic cracking units, hydrocracking units, gasoline treating units, and pumps, flanges, and other sources of fugitive emissions, and

2. Non-process emissions from wastewater treatment facilities, heaters and boilers.

3.2 BENZENE EMISSIONS FROM COAL COKING OPERATIONS

Coke was produced by 65 plants in the United States which had an annual coal capacity of 88,000,000 kkg (Mara and Lee, 1978). Of these 65, 10 (PEDCo, 1977) with an annual coal capacity of 25,600,000 kkg (Mara and Lee, 1978) produced benzene as a byproduct from light oil. According to A. D. Little (1977), half of the light oil produced was processed on-site (at 10 coke plants) to extract benzene. The "other half" was sold to petroleum refiners who extract benzene. Assuming

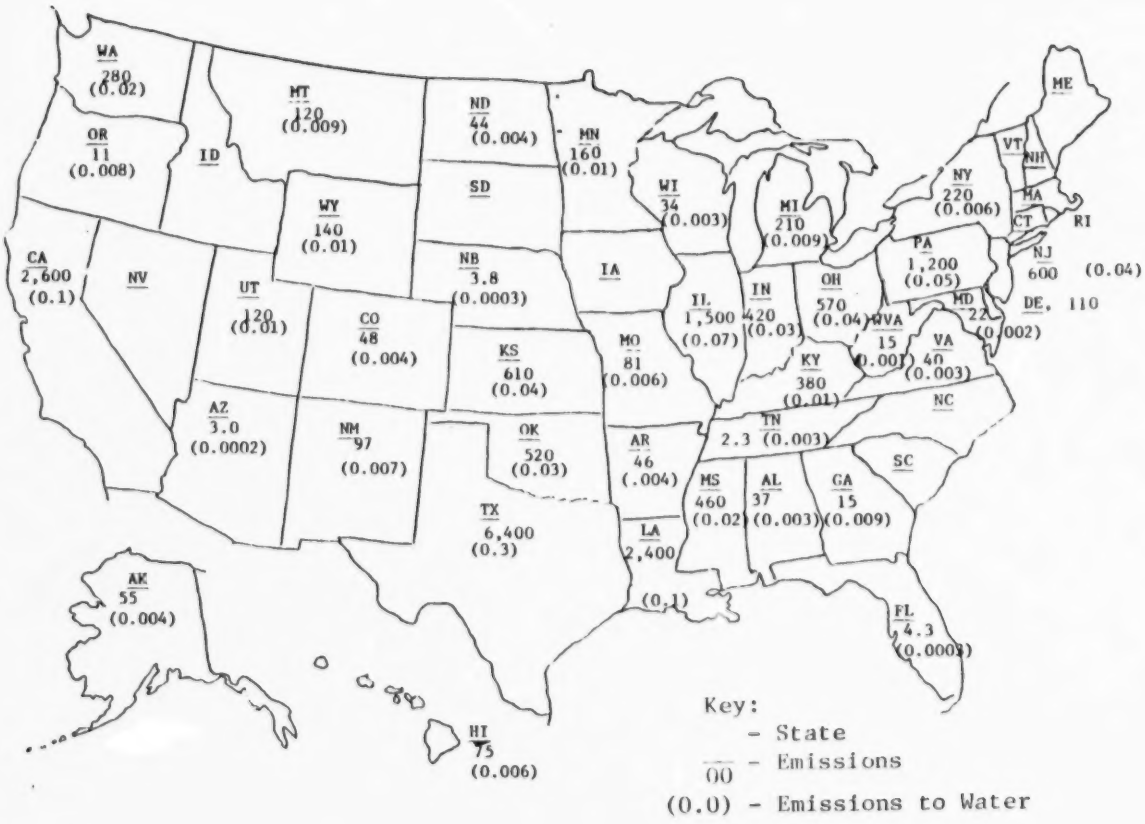


Figure 3.1 Benzene: Refinery Emissions by State (kkg)

Sources: Mara and Lee, 1978; Versar, 1977

that the 10 plants referred to by A. D. Little were the same 10 plants identified by PEDCo, and assuming that these 10 plants used all their light oil to produce benzene, it appears that the remaining 55 plants with an annual coal capacity of 62,700,000 kkg (Mara and Lee, 1978) produced the light oil sold to petroleum refiners. The yield of light oil is 3-4 gallons per kkg of coal carbonized (PEDCo, 1977). Applying this factor, the 10 benzene-producing coke plants had the capacity for producing and using approximately 100,000,000 gallons of benzene-containing light oil. The remaining 55 plants theoretically had the capacity for producing about 200,000,000 gallons of light oil. This is in sharp contrast to the 100,000,000 gallons (the "other half" of light oil production) that A. D. Little claims was sold to petroleum refineries. Some of the difference may be light oil which was used on-site in various processes (A. D. Little, 1977). It is unknown where the remainder of this difference went. If the 55 plants did not produce this unaccounted-for light oil, then the materials which could have gone into the light oil must have been used elsewhere or emitted to the environment. More data are needed to evaluate this potentially large source of emissions.

Possible sources of benzene emissions from coke oven operators, as indicated by PEDCo (1977), are:

1. Uncontrolled charging (i.e., placing the coal into the oven). Evaporation and coking of volatile components in the coal occurs upon the coal's contact with the hot oven floor. This is perhaps the greatest potential source of hydrocarbon (including benzene) emissions.

2. Topside emissions of fugitive benzene occurring from many sources including leakage from weakened refractory materials, ascension-pipe-elbow covers, leveling apertures, badly-fitted charging-hole covers, and collecting main pipe valves.

3. Coke pushing (the discharge of hot coke from the oven). This can be a major emission source unless the coal is completely carbonized.

4. Door leaks, on both the push and coke sides of the oven.

5. Waste-gas stacks if coal or coke escapes through leaks into areas between the oven and the heating flue.

6. Quenching (the flooding of pushed hot coke with a huge quantity of water to cool it rapidly). Much steam is produced, and emissions would depend upon how completely the coal was carbonized.

The literature revealed three factors for benzene emissions to air from coke oven operators. These are presented in Table 3.2.

The amount of benzene emitted to the air during coking operations was estimated using Walker's (1976) emission factor based on the following:

1. Full-capacity production requiring consumption of 88,000,000 kkg of coal (derived from Table C-1 in Mara and Lee, 1978).

2. The yield of coke from coal is 68.4 percent. The benzene emissions to air were estimated to be:

   (88,000,000 kkg coal)(68.4%)(9.80×10^{-4} kkg benzene/kkg coke produced)= 59,000 kkg benzene emitted.

Applying PEDCo's factor, the result would be:

(88,000,000 kkg coal)(7.8×10^{-5} kkg benzene/kkg coal used) = 6,900 kkg benzene emitted.

Applying Mara and Lee's factor in the same way, the result would be:

3,000 kkg benzene emitted

The Mara and Lee factor was also applied to capacities state-by-state to derive the distribution map of the 3,000 kkg benzene emissions from coke ovens. This map is presented in Figure 3.2.

No emission factors for benzene to water from coke ovens were revealed by the literature, therefore no emissions could be calculated.

The precision of emissions estimates based on Walker's emission factor was estimated to be $\pm$ a factor of 6, based on evaluation of his assumptions. The uncertainty is probably due almost entirely to the emission factor.

Table 3.2 Benzene Emission Factors - Coal Coking Operations

Source	Factor	Remarks
Walker (1976)	9.80×10^{-4} $\frac{\text{kkg benzene}}{\text{kkg coke produced}}$	
PEDCo (1977)	7.8×10^{-5} $\frac{\text{kkg benzene}}{\text{kkg coal used}}$	$(3.5 \times 10^{-3}$ $\frac{\text{kkg hydrocarbon}}{\text{kkg coal coked}})$(0.0223 fraction of benzene in total hydrocarbons) where $0.0223 = (\frac{0.776\% \text{ benzene in coke over year}}{34.8\% \text{ hydrocarbons in coke over year}})$
Mara and Lee (1978)	3×10^{-5} $\frac{\text{kkg benzene}}{\text{kkg coal used}}$	Estimated by multiplying the hydrocarbon emission factor (4.2 lbs/ton coal) by the fraction of benzene in the total hydrocarbon emission (0.0132). Based on EPA Document AP-42. The hydrocarbon emissions factor used here is different from the one used above. The factor for benzene content used here is different from that used above.

*Used here in deriving Figure 3.2.

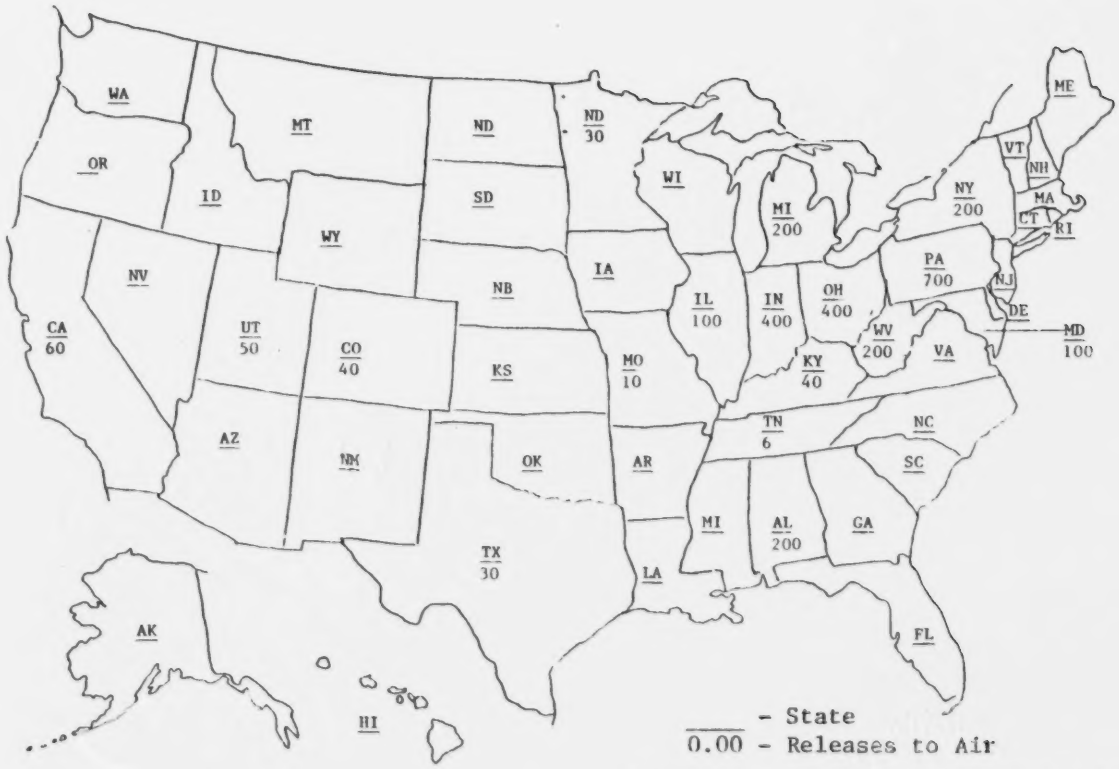


Figure 3.2 Benzene: Coke Oven Emissions by State (kkg)

Source: Mara and Lee, 1978

The uncertainty of the PEDCo emission factor was estimated by them to be ± a factor of 10. This would also be the uncertainty of the emissions calculated from the emission factor.

The uncertainty of Mara and Lee's emission factor could not be estimated. The factor had been obtained from EPA (1976).

3.3 INDIRECT PRODUCTION OF BENZENE FROM OIL SPILLS

Walker (1976) estimated benzene emissions to the oceans due to oil spills of all types using the following assumptions: 1) 11-12 x 10^9 lbs/year were discharged to the oceans. This included both natural and man-caused events. 2) Crude oil contains an average benzene concentration of 0.2 percent by weight (the range is reportedly 0.001 - 0.4 percent). Total benzene emissions to oceans were thus:

(11-12 x 10^9 lbs/year)(4.54 x 10^{-4} kkg/lb)(0.002 fraction benzene in oil) = 10-11 x 10^3 kkg benzene released to oceans

The uncertainty of the estimate is very large, however, The basis for the annual oil discharge value was not available, but the range of benzene contents for oils introduces a 400-fold uncertainty range by itself.

Versar (1977) estimated the gross annual discharge of benzene to U.S. waters, based on U.S. Coast Guard information on crude oil spills in 1976. Their estimate was based on the following: 1) The amount of crude oil lost to U.S. waters through spills in 1976 was reported to be 4,990,691 gallons. 2) Crude oil contains an average of 0.2 weight percent benzene (range: 0.001-0.4 percent). Benzene emissions were estimated to be:

(4,990,691 gallons)(7.211 lbs/gal benzene)(4.54 x 10^{-4} kkg/lb) x (0.002 fraction of benzene in oil) = 30 kkg benzene released to U.S. waters due to oil spills in 1976.

The uncertainty of this estimate is at least ± a factor of 400 (the range of benzene contents in crude oil).

This source of benzene emissions should be the subject of more detailed analysis if a Level II study is performed.

3.4 INDIRECT PRODUCTION OF BENZENE FROM VARIOUS SOURCES

Versar (1977) reported estimates of gross annual discharges of benzene to water in 1976. The results of these estimates are listed below:

Process	Estimated Gross Annual Discharge To Water, kkg
Nonferrous metals manufacturing (Al, Cu)	2.85
Ore mining (Pb, Zn)	1.1
Wood processing	0.4
Coal mining	141.1
Textile industry (subcategories 40 and 60)	2.51

3.5 SUMMARY

Benzene emissions from petroleum refineries were estimated to be 20,000 kkg to air and 1 kkg to water, the amount to land unknown.

Benzene emissions from coke oven operations were estimated to be 3,000 to 59,000 kkg to air with the amounts to water and land unknown.

Benzene emissions from oil spills were estimated to be 30 to 10-11 x 10^3 kkg to water (depending on the area being considered) with the amounts to air and land unknown.

Benzene emissions to water from other sources were estimated to be 2.85 kkg from non-ferrous metals manufacturing, 1.1 kkg from ore mining, 0.4 kkg from wood processing, 141.1 from coal mining and 2.51 kkg from the textile industry. Amounts emitted by these processes to air and land were unknown.

4.0 IMPORTS OF BENZENE

4.1 AMOUNT IMPORTED

Table 4.1 summarizes the amounts of benzene imported during the past five years:

TABLE 4.1 BENZENE IMPORTS, 1974-1979 (kkg)[1]

1979	1978	1977	1976	1975
232,000[2]	225,000	204,000	175,000	234,000

1. Source: Bureau of the Census, Department of Commerce
2. Based on extrapolation of January through October data for 1979.

4.2 EMISSIONS DUE TO IMPORTS

Emissions due to imports were interpreted as emissions due to unloading plus transport to the point of consumption. PEDCo (1977) estimated emission factors for these processes:

Process	Emission Factor
Marine loading	$2.0 \times 10^{-4} \frac{\text{kkg}}{\text{kkg unloaded}}$ (uncontrolled)
Transport	$1 \times 10^{-4} \frac{\text{kkg}}{\text{kkg transported/week}}$

In applying these emission factors due to 1978 imports, the following additional bases were used: (1) Emissions due to loading were 95 percent controlled at dockside. (2) The average time for imported benzene to be in transit was one week.

Emissions were then calculated to be:

$$\left[(225{,}000 \text{ kkg})(2.0 \times 10^{-4} \text{ kkg/kkg})(0.05)\right] + \left[(225{,}000 \text{ kkg})(1 \text{ week})(1 \times 10^{-4} \text{ kkg/kkg/week})\right] = 25 \text{ kkg benzene released per year due to importation}$$

We estimate the uncertainty of this emission to be $\pm$ a factor of 10, based on the difficulty of estimating emission factors for processes of this type.

4.2.1 Emissions to Air

Of the total emissions, it was judged that 50 percent would go to air and 50 percent to water. This estimate was based on the following: (1) Most "non-accident" emissions would be to air because of benzene's volatility. (2) Most emissions due to accidents would ultimately be to water, due to the fact that transfer operations are dockside and water would be used to hose down the area.

Therefore, air emissions = (25 kkg)(0.5) = 13 kkg benzene released to air due to importation.

4.2.2 Emissions to Water

By the reasoning presented in 4.2.1, the emissions to water due to importation of benzene would also be 13 kkg.

There would be no emissions of benzene to landfills or due to disposal of solid residues during importation.

5.0 CONSUMPTIVE USES AND EXPORTS OF BENZENE

The utilization of benzene can be broadly divided into consumptive uses and nonconsumptive uses. This chapter reports on emissions due to consumptive uses: processes in which benzene is chemically converted to another compound. Nonconsumptive uses, in which benzene is used as an end-product rather than as an intermediate, are discussed in Chapter 6.0. For the purposes of a materials balance, exports are considered consumptive uses because the chemical is permanently removed from the U.S. "inventory" by this process. Therefore, exports are also discussed in this chapter.

5.1 CONSUMPTIVE USES--TOTALS

5,389,000 kkg were estimated to have been consumptively used in 1978. This total was derived in Table 5.1. The main use of benzene was as a chemical intermediate in the synthesis of other organics.

5.2 CATEGORIES OF USE

The major compounds derived from benzene in 1978 are listed in Table 5.1. In addition, minor uses are included in the benzene Environmental Flow Diagram, Appendix A. Ethylbenzene synthesis was by far the largest consumer of benzene, as it has been historically (See Table 5.2 at end of chapter for data on the years 1975-1979). The data on these two tables were based on USITC reports. Their uncertainty is not known, but it is estimated to be small (less than $\pm$20%).

5.3 EMISSIONS BY CATEGORY OF USE

5.3.1 Consumption of Benzene by Ethylbenzene Synthesis

5.3.1.1 Processes, Producers, and Locations

Approximately 90-95% of ethylbenzene production is carried out by alkylation of benzene with ethylene (Versar, 1979; Weissermel and Arp, 1978; A.D. Little, Inc., 1977):

TABLE 5.1 CONSUMPTIVE USES OF BENZENE (1978)

Use	kkg Produced[1]	kkg Benzene Required[3]
Ethylbenzene	3,803,000	2,890,000
Cumene	1,533,000	1,058,000
Cyclohexane	1,057,000	811,000
Nitrobenzene[2]	261,000	170,000
Maleic anhydride	155,000	161,000[4]
Chlorobenzenes (mono- plus di-)	171,000	133,000
Detergent Alkylate (linear plus branched)	330,000[5]	132,000
Anthraquinone	17,000[6]	23,000
Biphenyl	29,000	11,000
		5,389,000

1. USITC figures except as noted.
2. Includes nitrobenzene destined for aniline synthesis (96%), plus non-aniline usage (4%).
3. Conversion factors from Neufeld et al., 1978.
4. This assumes that 81% of maleic anhydride was made from benzene (PEDCo, 1978).
5. Derived from 1978 USITC production figure for straight-chain alkylbenzenes (239,000 kkg) by assuming a ratio linear/branched = 2.64 (Neufeld et al., 1978).
6. Total Vat Dye production (USITC, 1978, Neufeld et al., 1978).

Ethylbenzene
b.p. 136°C

The process is carried out in either liquid- or vapor-phase, using an excess of benzene to minimize diethylbenzene byproducts. It is not known whether the liquid- or vapor-phase process predominates. The isolation of ethylbenzene as a byproduct of xylenes and cumene production accounts for the rest of ethylbenzene production. Almost all ethylbenzene is used for the subsequent production of styrene monomer (Versar, 1979). Figure 5.1 is a process flow diagram for ethylbenzene synthesis.

Figure 5.2 lists ethylbenzene producers, production capacities, and plant locations. Of the 3,547,000 kkg of 1976 benzene-consuming capacity listed, at least 75% is located along the Gulf Coast (Channelview, TX, and Welcome, LA, could not be located on the maps used). The plant capacity data were from SRI (1977). It was difficult to assess the reliability of these data. Comparison of 1976 benzene consumption due to ethylbenzene synthesis (Table 5.2) with the amount of benzene required for full-capacity ethylbenzene synthesis (Figure 5.1) showed that ethylbenzene synthesis was at 67% of capacity in 1976.

5.3.1.2 Amount of Benzene Consumed

2,890,000 kkg of benzene were used for the synthesis of ethylbenzene in 1978 (Table 5.1). This value was obtained by the operation: (kkg ethylbenzene produced) (conversion factor). The conversion factor used was 0.76. This factor is equal to the ratio of molecular weights (benzene/ethylbenzene) ÷ the percent theoretical yield. The latter was estimated to be 97% by A.D. Little, Inc. (1977). The uncertainty in the estimate of the amount of benzene consumed during ethylbenzene synthesis was ±20%.

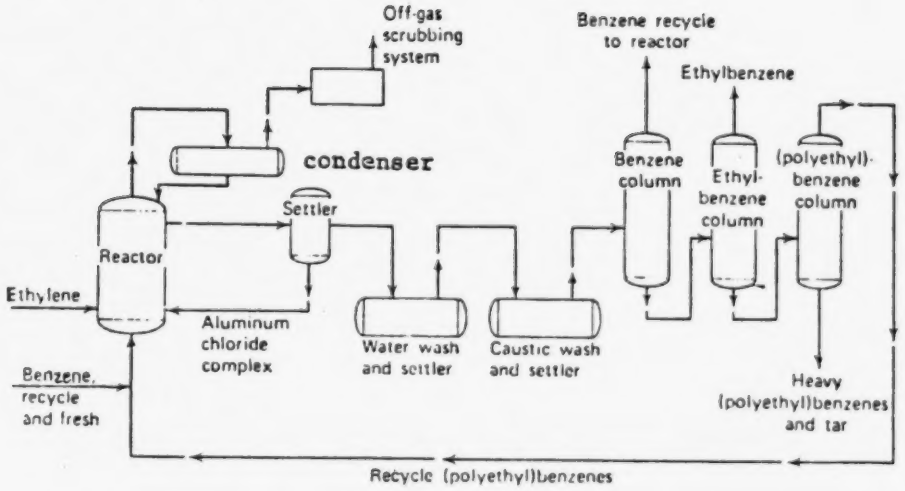


Figure 5.1 The Manufacture of Ethylbenzene Employing Aluminum Chloride as Catalyst

5.3.1.3 Benzene Emissions Due to Ethylbenzene Synthesis

5.3.1.3.1 Generated Emissions to Air

Previous studies have proposed emission factors for release of benzene to the air due to consumption processes. One approach was to set an upper limit on emissions by relegating all unaccounted-for benzene to this category (Howard et al., 1974). An average yield of 97% of theoretical has been estimated for benzene alkylation (A. D. Little, 1977). Applying this information to 1978 ethylbenzene synthesis would give:

$$(3{,}803{,}000 \text{ kkg ethylbenzene produced})(0.03 \text{ fraction of ethylbenzene lost})\left(\frac{78 \text{ g benzene used}}{106 \text{ g ethylbenzene used}}\right) = 84{,}000 \text{ kkg benzene unaccounted for}$$

A second approach was to estimate an overall emission factor for total benzene consumption. Patterson et al. (1976) used the value 0.005 kkg/kkg benzene consumed, although the origin of the value is unclear. Application of this emission factor to 1978 consumption for ethylbenzene production gives:

(2,890,000 kkg benzene consumed)(0.005 kkg/kkg) = 14,000 kkg benzene emissions generated for release to air during ethylbenzene synthesis.

A third emission factor was obtained from Versar (1979), based on PEDCo Environmental (1977). In Versar (1979), airborn emissions were estimated to be 1200 kkg for production of 1,790,000 kkg ethylbenzene in 1976. The emission factor calculated from these values was:

$\frac{1{,}200 \text{ kkg}}{1{,}790{,}000 \text{ kkg}} = 6.7 \times 10^{-4}$ kkg/kkg produced. This was equivalent to $(6.7 \times 10^{-4}$ kkg/kkg ethylbenzene produced$)\left(\frac{106 \text{ kkg ethylbenzene produced}}{78 \text{ kkg benzene used}}\right)$ $= 9.1 \times 10^{-4}$ kkg/kkg benzene used.

Application of this emission factor to 1978 benzene consumption for ethylbenzene synthesis gave:

$(2{,}890{,}000$ kkg benzene consumed$)(9.1 \times 10^{-4}$ kkg/kkg benzene consumed) = 2600 kkg benzene emissions generated for release to air.

These emissions are summarized in Table 5.3.

Of the three values, the 84,000 kkg estimate is an absolute maximum and is undoubtedly too high. By assuming either recycling or destruction of a large proportion of the unaccounted-for benzene, lower emissions are estimated. Pending evaluation of further information, emissions of benzene to air during ethylbenzene synthesis will be

Locations (1976)

COMPANIES AND CAPACITIES (1976)[1]

Map No.	Company	Plant Location	Ethylbenzene Capacity, kkg/yr	Full Capacity Benzen Requirement,* kkg/yr
1.	American Petrofina	Big Spring, TX	20,000	15,000
2.	ARCO/Polymers, Inc.	Port Arthur, TX	200,000	152,000
3.	Cos-Mar, Inc.	Carville, LA	689,000	524,000
4.	Dow Chemical	Freeport, TX	846,000	643,000
5.	Dow Chemical	Midland, MI	249,000	189,000
6.	El Paso Nat. Gas	Odessa, TX	125,000	95,000
7.	Foster Grant	Baton Rouge, LA	440,000	334,000
8.	Gulf Oil Chem.	Welcome, LA	249,000	189,000
9.	Joc Oil Co.	Houston, TX	NA	NA
10.	Monsanto Co.	Alvin, Tx	23,000	17,000
11.	Monsanto Co.	Texas City, Tx	658,000	500,000
12.	Oxirane Chem	Channelview, TX	544,000	413,000
13.	Phillips Petroleum	Phillips, TX	NA	NA
14.	Standard Oil (Ind)	Texas City, TX	429,000	326,000
15.	Sun Oil Co.	Corpus Christi, TX	43,000	33,000
16.	Union Carbide	Seadrift, TX	154,000	117,000
		SUM	4,669,000	3,547,000

1. Arthur D. Little, Inc., 1977.

2. Conversion factor used was 0.76 kkg benzene/kkg ethylbenzene (Arthur D. Little, Inc., 1977). This value is the ratio of molecular weights (benzene/ethylbenzene) ÷ the % theoretical yield (assumed to be 97% in the reference cited above).

Figure 5.2 Production of Ethylbenzene from Benzene

Table 5.3 Summary of Estimated Benzene Emissions to Air Due to Ethylbenzene Synthesis

Method Used	Emission Factor (kkg/kkg benzene consumed)	Emissions to Air, 1978, kkg	Reference
Sum of Unaccounted-for Benzene	--	84,000	Howard et al., 1974
Estimate Emission Factor (basis not stated)	5×10^{-3}	14,000	Patterson et al., 1976
Estimate Emission Factor (from emissions and consumption data)	9.1×10^{-4}	2,600	Versar, 1979

expressed as the range 2,600 - 14,000 kkg.

5.3.1.3.2 Generated Emissions to Water

The amount of benzene generated for release to water was estimated to be 345 kkg in 1976 (Versar, 1977). Ethylbenzene production that year was 1,790,000 kkg; the emission factor was therefore:

$345 \div 1{,}790{,}000 = 1.9 \times 10^{-4}$ kkg benzene released/kkg ethylbenzene produced.

Application of this emission factor to 1978 ethylbenzene production yields:

(3,803,000 kkg ethylbenzene produced)$(1.9 \times 10^{-4}$ kkg/kkg) = 720 kkg benzene released to water due to ethylbenzene production.

This value has an estimated uncertainty of $\pm$ a factor of 10, since it was based on estimates of both the emission factor and the fraction of generated emissions entering water. The main source of these water emissions was probably scrubber effluents.

5.3.1.3.3 Emissions Due to Disposal of Solid Residues

It was not possible to estimate emissions of benzene in solid residues. In order to estimate these emissions, it would be necessary to know: (1) the rate of production of benzene-containing sludges, (2) the weight % benzene in the sludge, and (3) the method of disposal of the sludge (landfill, incineration).

5.3.1.3.4 Carry-Over of Benzene during Ethylbenzene Synthesis

Data were not available to permit estimation of benzene contamination in ethylbenzene. This would appear to be an important topic for a Level II study.

5.3.2 Consumption of Benzene by Cumene Synthesis

5.3.2.1 Processes, Producers, Locations

All chemical-grade cumene produced in the U.S. at present is made by the alkylation of benzene with propylene (Peterson, 1979). The basic reaction in this process is:

cumene

Most cumene is produced by the Solid Phosphoric Acid Process, as shown in Figure 5.3. Benzene and propylene are reacted at elevated temperatures and pressures in the presence of an acidic catalyst (Peterson, 1979).

Figure 5.4 shows the producers and locations for 1978 production.

5.3.2.2 Amounts Manufactured

According to USITC (1979), 1,533,000 kkg of cumene were produced in 1978. The amount of benzene required to synthesize this amount of cumene was estimated by using a conversion factor. The factor for calculating benzene consumption was 0.69 kkg benzene required/kkg cumene produced (SRI, 1977). This value is equal to the ratio (molecular weight benzene/molecular weight cumene) ÷ theoretical yield. A 94% yield was estimated by SRI for cumene synthesis. Applying this conversion factor to the ITC production data for cumene production yielded:

(1,533,000 kkg)(0.69) = 1,058,000 kkg benzene required for cumene production in 1978.

5.3.2.3 Emissions of Benzene Due to Production of Cumene

Data on benzene emissions during cumene synthesis for 1978 were not found in any available sources. Based on 1978 USITC production data and an emission factor from PEDCo (1977) on benzene emissions from the production of cumene in 1976, emissions were calculated to be:

(1,533,000 kkg) x (0.25×10^{-3} kkg/kkg) = 380 kkg benzene released during 1978.

This 0.25×10^{-3} kkg/kkg emission factor was for fugitive emissions. There was no information to permit estimation of the accuracy of this factor.

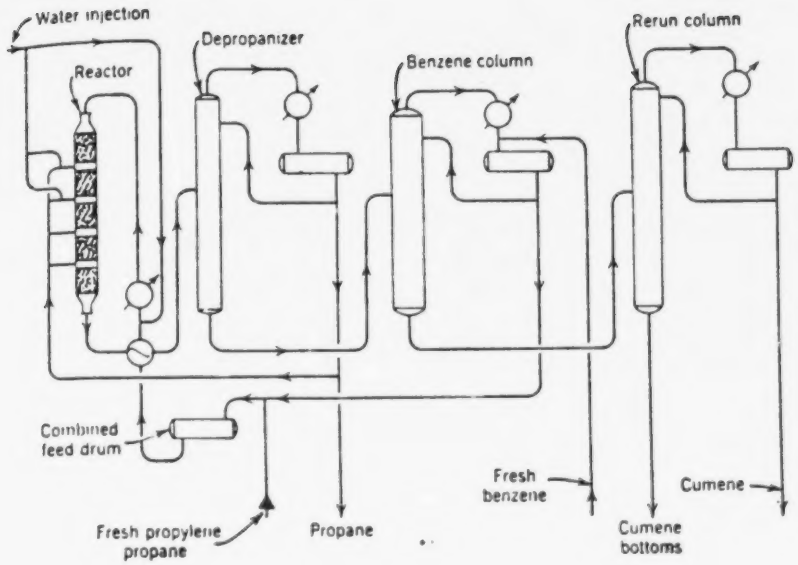


Figure 5.3 Solid Phosphoric Acid Process for Cumene Production

Source: A.D. Little, Inc., 1977

PRODUCERS AND BENZENE REQUIREMENTS[1]

		Cumene Production kkg[2]	Benzene Used kkg[3]
1.	Amoco Oil Co., Texas City, TX	9,000	6,000
2.	Ashland Oil Co., Catlettsburg, KY	118,000	81,000
3.	Chevron Oil Co., El Segundo, CA	27,000	19,000
4.	Clark Oil Co., Blue Island, IL	35,000	24,000
5.	Coastal States Gas Co., Corpus Christi, TX	44,000	30,000
6.	Dow Chemical, Midland, MI	3,000	2,000
7.	Georgia Pacific Corp., Houston, TX	221,000	152,000
8.	Getty Oil Co., El Dorado, TX	40,000	28,000
9.	Gulf Oil, Philadelphia, PA	133,000	92,000
10.	Gulf Oil, Port Arthur, TX	130,000	90,000
11.	Marathon Oil Co., Texas City, TX	56,000	39,000
12.	Monsanto Chemical Co., Chocolate Bayou, TX	206,000	142,000
13.	Shell Oil Co., Deer Park, TX	206,000	142,000
14.	Sun Petroleum Products Co., Corpus Christi, TX	68,000	47,000
15.	Texaco, Inc., Westmill, NJ	44,000	30,000
16.	Union Carbide Corp., Ponce, PR	189,000	130,000
		1,529,000[4]	1,034,000[4]

[1]Source: Numbers were extrapolated from ITC 1978 Production data by using 1978 Cumene Capacity figures from Peterson 1979 for all plants except 1976 Cumene Capacity figures for Dow Chemical and Marathon Oil (A.D. Little, Inc., 1977). These numbers were multiplied by 0.65 which was derived by dividing 1978 ITC production by total cumene capacity (Peterson, 1979):

$$\frac{1,533,000 \text{ kkg}}{2,352,000 \text{ kkg}} = 0.65$$

[2]The cumene production was directly proportional to capacity of each plant and was not actual production.

[3]Benzene use was calculated by applying the conversion factor for benzene consumption in the production of cumene: 0.69 kkg benzene per kkg of cumene produced. This conversion factor was taken from SRI (1977) and is also used in other sources.

[4]These totals do not match the totals in the text due to rounding.

Figure 5.4 Cumene Production: Producers and Locations

5.3.2.3.1 Emissions to Air

There were no data on exact amounts of the emissions of benzene into the air from the production of cumene. It was assumed that almost all emissions are to the air. This assumption was based on the volatility of benzene, and the fact that the reaction is carried out at elevated temperature or in the vapor phase (A.D. Little, Inc., 1977). More information is needed to properly determine the quantities of benzene emitted to the air from cumene production.

5.3.2.3.2 Emissions to Water

While no data on the exact amounts of emissions of benzene to water from the production of cumene are available, it can be assumed that only a small percentage of the total emissions are to water (see above). More information is needed to properly determine the quantities of benzene emitted to the water from cumene production.

5.3.2.3.3 Emissions Due to Disposal of Solid Residues

No information on the disposal of solid residues was provided. In order to estimate these emissions, it would be necessary to know: (1) the rate of formation of benzene-containing residues, (2) the weight % benzene in the residues, and (3) the method of residue disposal (incineration, landfill).

5.3.2.3.4 Carry-Over of Benzene into Product

Carry-over of benzene as a contaminant of cumene may be a significant source of emissions, and should be addressed in a Level II study.

5.3.3 Consumption of Benzene by Cyclohexane Synthesis

5.3.3.1 Processes, Producers, Locations

Three processes are used in the synthesis of cyclohexane:

1) Hydrogenation of benzene,
2) Isolation from crude gasoline by fractional distillation, and
3) Isolation from crude gasoline by fractional distillation with

simultaneous isomerization (Weissermel and Arpe, 1979).

Of these methods, hydrogenation of benzene accounted for 80-85% of cyclohexane production, while the other two accounted for the remaining 15-20%.

Hydrogenation of benzene produces cyclohexane of high purity, over 99%, as compared to 85% for the fractionating process and 98% for the fractionation combined with isomerization (A.D. Little, Inc., 1977).

The reaction equation for the catalytic hydrogenation of benzene is shown below.

Benzene

Cyclohexane
b.p. 80°C

The process is carried out at elevated temperature in either liquid- or vapor-phase, at a hydrogen pressure of 20-40 atm (Weissermel and Arpe, 1978). Figure 5.5 shows the industrial process flow chart for liquid-phase benzene hydrogenation.

Several reactors are used to progressively improve the conversion to cyclohexane until residual amounts of benzene and methylcyclopentane are reduced to less than 100 ppm.

Figure 5.6 shows the location of U.S. cyclohexane producers.

5.3.3.2 Amounts Produced

1978 production data are also shown in Figure 5.6. The benzene requirement was calculated by using the conversion factor 0.93 kkg benzene required per kkg cyclohexane produced (Neufeld et al., 1978). Cyclohexane production by each plant in 1978 was estimated by assuming that the quantity produced was proportional to the fraction of the total U.S. production capacity that it contributed in 1976:

1978 cyclohexane production by a plant = (Total U. S. production of cyclohexane in 1978) (% of total production capacity contributed by plant in 1976)

Cyclohexane production figures were taken from USITC.

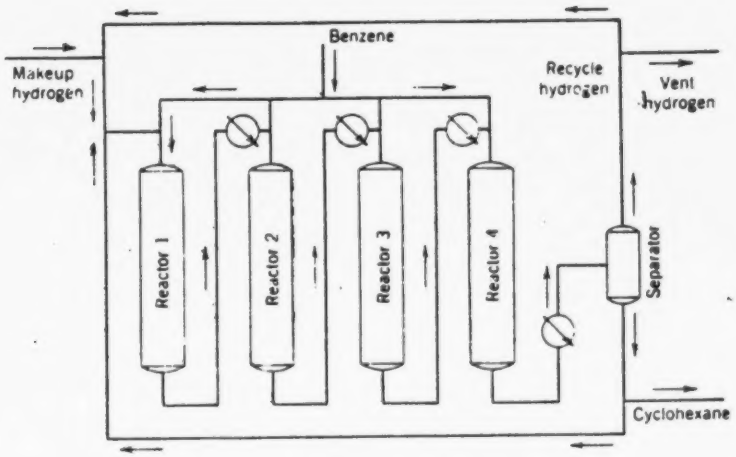


Figure B-11 Hydrogenation of Benzene

PRODUCERS[1] AND BENZENE REQUIREMENTS

Map No.	Company	Location	kkg Cyclohexane Produced[2]	kkg Benzene Used[3]
1	Amer. Petrofina	Big Springs, TX	31,000	29,000
2	Commonwealth Oil	Penuelas, PR	101,000	94,000
3	Exxon Chem.	Baytown, TX	101,000	94,000
4	Gulf Oil Chem.	Port Arthur, TX	84,000	78,000
5	Phillips Chem.	Sweeney, TX	216,000	106,000[4]
6	Phillips Petroleum	Guayama, PR	228,000	212,000
7	Sun Oil Co.	Tulsa, OK	51,000	47,000
8	Texaco, Inc.	Port Arthur, TX	101,000	94,000
9	Union Oil Calif.	Beaumont, TX	87,000	81,000
10	Union Pacific	Corpus Christi, TX	56,000	52,000
		Total	1,056,000	887,000

[1]Source: SRI, 1976.

[2]Derived from individual plant capacities (A.D. Little, Inc., 1977) using the assumption that a plant's percent contribution to total production in 1978 equals the plant's percent contribution to total capacity in 1976. Total 1978 production was from USITC.

[3]Estimated using the conversion factor 0.93 kkg benzene used/kkg cyclohexane produced (Neufeld et. al., 1978).

[4]Benzene feedstock was estimated to account for 47-59% of plant production (A.D. Little, Inc., 1977). The average value (53%) was used as the percent of production derived from benzene.

Figure 5.6 Production of Cyclohexane from Benzene, 1978

5.3.3.3 Benzene Emissions Due to Cyclohexane Synthesis

Benzene emissions would be expected to be negligible during cyclohexane production from simple fractionation of natural gasoline (A.D. Little, Inc., 1977). This is because benzene is present only as a minor constituent of the crude gasoline and its concentration would only be measured at trace levels. The same analysis applies to the fractionation/isomerization method of cyclohexane synthesis.

An emission factor of 0.0028 kkg of benzene emitted per kkg of cyclohexane produced was cited by Mara and Lee (1978). They regarded it as an order of magnitude estimate. In the absence of specific information on the applicability of this emission factor, it was assumed that it describes an average of the three manufacturing processes with no attempt made to distinguish among these.

To estimate atmospheric benzene emissions, total U.S. cyclohexane production for 1978 (Figure 5.6) was multiplied by 0.0028 kkg/kkg:

(1,056,000 kkg cyclohexane produced)(0.0028 kkg/kkg product) = 3,000 kkg benzene emissions due to cyclohexane synthesis.

5.3.3.3.1 Emissions to Air

Figure 5.5 indicated that the only vent in the otherwise closed reactor sequence was the gas vent for hydrogen. Any other losses would be due to leaks, spills, and catalyst regeneration. We estimated that 99% of emissions were to the air. Application of this percentage to total emissions estimated in 5.3.3.3 yielded:

(3,000 kkg benzene emitted) x (0.99 fraction to air) = 2970 kkg benzene released to air during cyclohexane synthesis.

The uncertainty of this value was estimated to be the same as that of the emission factor: $\pm$ a factor of 10.

5.3.3.3.2 Emissions to Water

As discussed above, emissions to water would be:

(3,000 kkg benzene emitted) x (0.01 fraction to air) = 30 kkg benzene released to water during cyclohexane synthesis.

5.3.3.3.3 Benzene Emissions to Land

Neither qualitative nor quantitative data concerning benzene emission to land as a result of cyclohexane manufacture were available.

5.3.3.3.4 Carry-Over of Benzene into Product

Hydrogenation of benzene produces a cyclohexane with over 99% purity. Weissermel and Arpe (1978) indicated that where a finishing reactor was used in conjunction with a series of reactors, hydrogenation of benzene could be complete enough so as to leave the cyclohexane end product with less than 100 ppm (0.01% by mass) of benzene and methylcyclopentane contamination. Also, A.D. Little, Inc. (1977) estimated that from 0-0.5% benzene by volume may be detected in cyclohexane. The amount of this carry-over that is ultimately released could not be predicted due to the lack of information on cyclohexane uses.

While cyclohexane production from fractionation of crude gasoline and simultaneous isomerization has a 98% yield, neither the quantity of benzene residue nor its rate of release could be ascertained.

According to A.D. Little, Inc. (1977) (who cited R.M. Stephenson, Introduction to the Chemical Process Industries), the 15% impurities in cyclohexane extracted from gasoline (Section 5.3.3.1) contained benzene, 2,2-dimethylpentane, and 2,4-dimethylpentane. However, A.D. Little, Inc. (1977) also reported that the plant manager at Borger, Texas stated to them in a personal communication that no benzene existed in the 85% cyclohexane end-product. No information was available to resolve this conflict nor has the possible release of these contaminants been studied.

5.3.4 Consumption of Benzene by Maleic Anhydride Synthesis

5.3.4.1 Producers, Processes, Locations

Maleic anhydride is produced by the catalytic oxidation of benzene according to the equation:

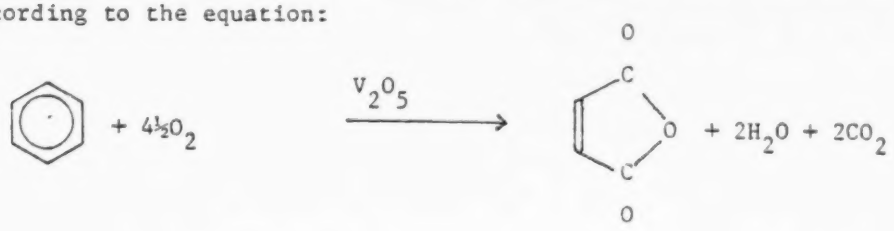


Figure 5.7 shows the industrial flow chart for this process.

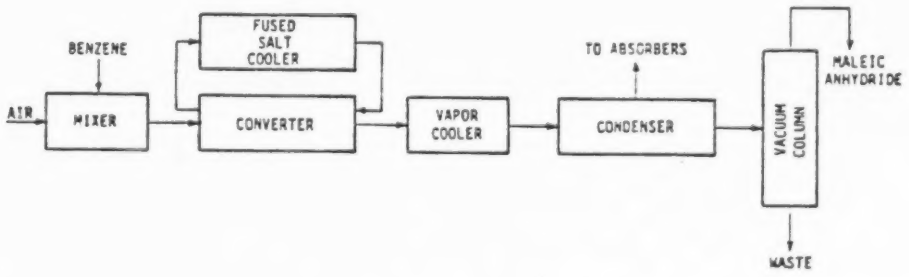


Figure 5.7 Flow Chart for Maleic Anhydride Synthesis

Figure 5.8 shows the locations and benzene requirements of maleic anhydride producers.

5.3.4.2 Amounts Produced

USITC reported a production of 155,000 kkg maleic anhydride in 1978. The corresponding benzene requirement was estimated based on the following information: 1) Theoretically, 78 g benzene yields 110 g maleic anhydride. 2) In practice, a 55% yield is achieved (A.D. Little, Inc., 1977). 3) 81% of maleic anhydride is currently derived from benzene (PEDCo, 1978). The factor for conversion of maleic anhydride production to benzene consumption was

$$\left[\frac{78 \text{ g benzene}}{110 \text{ g maleic anhydride}}\right]\left[\frac{1}{0.55 \text{ yield}}\right](0.81 \text{ fraction from benzene})$$

= 1.04 kkg benzene used/kkg maleic anhydride produced.

This conversion factor was used in Figure 5.8. The total estimated benzene consumption for maleic anhydride synthesis in 1978 was 161,000 kkg.

5.3.4.3 Emissions Due to Maleic Anhydride Synthesis

5.3.4.3.1 Emissions to Air

The main source of benzene emissions during maleic anhydride synthesis was reported to be the condenser vent (labeled "to absorbers" in Figure 5.7) (PEDCo, 1977). PEDCo (1977) cites the results of a 1972 emissions inventory showing emission factors for controlled plus uncontrolled emissions from this vent to be 0.06 - 0.20 kkg/kkg maleic anhydride produced. Also cited was a report by Monsanto Research containing an emission factor of 0.0967 kkg/kkg product for controlled emissions from a maleic anhydride plant. In order to present a worst-case estimate, the emission factor 0.20 kkg/kkg product was employed to estimate 1978 benzene emissions. Conversion of this value to kkg benzene released/kkg benzene used yields:

$$(0.20 \text{ kkg/kkg product}) \times \left(\frac{1 \text{ kkg product}}{1.04 \text{ kkg benzene used}}\right) = 0.21 \text{ kkg/kkg benzene used.}$$

Application of this emission factor to 1978 benzene consumption (Figure 5.8) yields:

(161,000 kkg)(0.21 kkg/kkg) = 34,000 kkg benzene released due to maleic anhydride synthesis in 1978.

Based on the 3.7 - fold range of the literature emission factors and the judgment that emissions have probably decreased since 1972 due to added controls, the uncertainty of the 1978 emissions to air was estimated to be + 10%, - 90%.

5.3.4.3.2 Emissions to Water

The synthesis of maleic anhydride is of necessity an anhydrous process, since the anhydride is destroyed by hydrolysis. Thus, any loss of benzene to water would be indirect (scrubber effluents, leaks). Versar (1979) cited Versar (1977) as the source of an estimated aqueous emission of 8 kkg in 1976 due to maleic anhydride synthesis. Consulting the latter

source, however, failed to reveal any mention of benzene emissions due to maleic anhydride synthesis. Thus, although the low estimated aqueous emission was qualitatively reasonable, its origin was unclear. No uncertainty range was assigned to this value.

5.3.4.3.3 Emissions Due to Disposal of Solid Residue

No data were available on benzene emissions due to disposal of solid residues. The vacuum column waste stream would be expected to contain no benzene, because benzene has a lower boiling point than maleic anhydride and would exit the column with the product. Based on this brief analysis, it was estimated that emissions of benzene due to disposal of solid residues from maleic anhydride synthesis were negligible.

5.3.4.3.4 Carry-Over of Benzene into Product

Information was not readily available on benzene contamination of maleic anhydride product. It would be necessary to obtain analyses of maleic anhydride batches in order to evaluate this possibility.

5.3.5 Consumption of Benzene by Nitrobenzene Synthesis

5.3.5.1 Processes, Producers, and Locations

Synthesis of nitrobenzene is carried out by the nitration of benzene:

The process is carried out in liquid phase. Almost all nitrobenzene is used in the subsequent production of aniline (Versar, 1979). Figure 5.9 is a process flow diagram for nitrobenzene synthesis.

Figure 5.10 lists the nitrobenzene producers, production capacities, and plant locations. The data are for 1976. Comparison of the full capacity benzene requirement (356,000 kkg; Figure 5.10) with the 1976 consumption of benzene for nitrobenzene synthesis (169,000 kkg; Table 5.2) indicates that nitrobenzene plants were operating at 48% of capacity that year.

COMPANIES AND BENZENE CONSUMPTION[1]

Map No.	Company	Location	1978 Benzene Consumption, kkg[2]
1.	Allied Chemical	Moundsville, WV	20,000
2.	Koppers Co.	Bridgeville, PA	11,300
3.	Monsanto Co.	St. Louis, MO	27,500
4.	Petro-Tex Chem.	Houston, TX	16,700
5.	Reichold Chem.	Elizabeth, NJ	10,000
6.	Reichold Chem.	Morris, IL	20,000
7.	Tenneco, Inc.	Fords, NJ	8,700
8.	U. S. Steel	Neville Island, PA	26,700
9.	Ashland Oil	Neal, WV	20,000
		SUM	161,000

1. Source: A. D. Little, Inc., 1977.

2. The conversion factor used was 1.04 kkg benzene used/kkg maleic anhydride produced (see section 5.3.4.2). Total benzene consumption for 1978 was allocated to individual plants in proportion to their 1976 capacities (A. D. Little, Inc., 1977).

Figure 5.8 Maleic Anhydride Producers and Locations

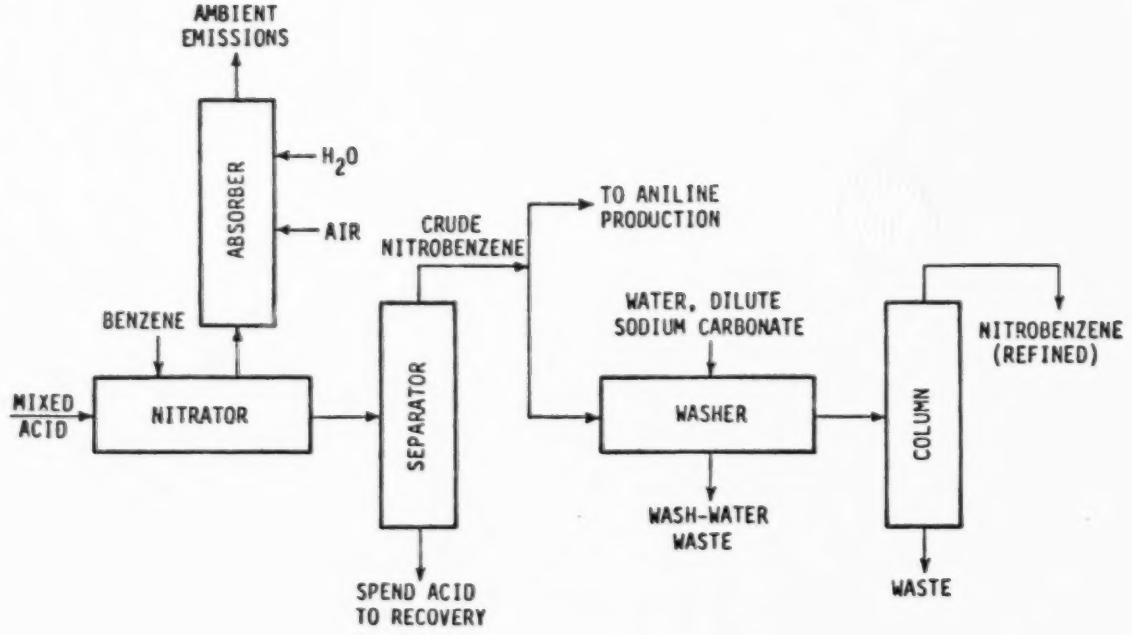


Figure 5.9 Process Flow for Nitrobenzene Synthesis

LOCATIONS (1976)

COMPANIES AND CAPACITIES (1976)[1]

Map No.	Company	Plant Location	Nitrobenzene Capacity, kkg/yr	Full Capacity Benzene[2] Requirement, kkg/yr
1.	Allied Chemical	Moundsville, WV	25,000	16,000
2.	American Cyanamid	Bound Brook, NJ	38,000[3]	25,000
3.	E. I. duPont	Beaumont, TX	141,000	92,000
4.	E. I. duPont	Gibbstown, NJ	91,000	59,000
5.	First Mississippi Corp.	Pascagoula, MS	61,000[4]	40,000
6.	Morbay Chemical	New Martinsville, WV	61,000	40,000
7.	Monsanto Co.	Sauget, IL	5,000	3,000
8.	Rubicon Chemicals	Geismar, LA	124,700[5]	81,000
		SUM	546,700	356,000

1. Source: Arthur D. Little, Inc., 1977.
2. Based on the conversion factor 0.65 kkg benzene required/kkg nitrobenzene (Neufeld, et al., 1978).
3. Plant on standby until early 1978.
4. Planned expansion will double capacity.
5. Effective during 1976.

Figure 5.10 Production of Nitrobenzene from Benzene

5.3.5.2 Amount of Benzene Consumed

170,000 kkg of benzene were used for the synthesis of nitrobenzene in 1978. This value was obtained by the operation:

(kkg nitrobenzene produced)(conversion factor)

The conversion factor used was 0.65 kkg benzene used/kkg nitrobenzene produced. This factor was equal to the ratio of molecular weights (benzene/nitrobenzene) ÷ the % theoretical yield. The latter was estimated to be 97% by Neufeld et al., 1978. The uncertainty in the estimate of the amount of benzene consumed during nitrobenzene synthesis was ± 20%.

5.3.5.3 Benzene Emissions Due to Nitrobenzene Synthesis

5.3.5.3.1 Emissions to Air

Previous studies have estimated values for release of benzene due to nitrobenzene synthesis. The results are summarized in Table 5.4.

Patterson et al. (1976) apply an emission factor of 5×10^{-3} kkg/kkg (0.5%) to benzene-consuming processes. This value, in turn, is based on "available data in (Compilation of Air Pollutant Emission Factors, U.S. EPA Report AP-42, April, 1973) and emission data for other similar processes." Applying this emission factor to 1978 benzene use for nitrobenzene synthesis yields:

(170,000 kkg) (5×10^{-3} kkg/kkg) = 900 kkg benzene released to air during nitrobenzene synthesis .

Table 5.4 Summary of Estimated Benzene Emissions to Air Due to Nitrobenzene Synthesis

Method Used	Emission Factor	1978 Emissions to Air, kkg	Reference
General Emission Factor for Benzene Consumption	5×10^{-3} kkg/kkg benzene used	900	Patterson, et al., 1976
Measured Emissions at Reactor Vent	8.3×10^{-3} kkg/kkg product	2200	Process Research, Inc., 1972
Estimate Emission Factor from Emissions and Consumption Data	1.1×10^{-2} kkg/kkg benzene used	1900	Versar, 1979

Because of the lack of background information, it was not possible to evaluate the uncertainty of this emission.

A second emission estimate was based on an emission factor of 8.3×10^{-3} kkg benzene released to air/kkg of nitrobenzene produced (Process Research, Inc., 1972). This emission factor was measured at the reactor absorber vent of a benzene nitration plant, and is characterized by the authors as being based on little or no census or experimental data. No uncertainty range was associated with the number. Application of the emission factor to 1978 nitrobenzene production yields:

$$(261{,}000 \text{ kkg})(8.3 \times 10^{-3} \text{ kkg/kkg product}) = 2200 \text{ kkg benzene released to air during nitrobenzene synthesis.}$$

A third estimate was that of Versar, 1979. Based on PEDCo Environmental (1977), they calculated airborne emissions of 3390 kkg for consumption of 302,000 kkg benzene. This yields an emission factor of

$$(3390 \text{ kkg}/302{,}000 \text{ kkg} = 1.1 \times 10^{-2} \text{ kkg/kkg}).$$

Application of this emission factor to 1978 benzene consumption yields:

$$(170{,}000 \text{ kkg})(1.1 \times 10^{-2} \text{ kkg/kkg used}) = 1900 \text{ kkg benzene released to air during nitrobenzene synthesis.}$$

No uncertainty range could be assigned to this value.

The three values tabulated varied over a range of a factor of 2.6. Since no value was clearly superior, the highest emission (2200 kkg) was selected in order to present a "worst case" estimate.

5.3.5.3.2 Generated Emissions to Water

No information was readily available on benzene emissions to water during nitrobenzene synthesis. Because of benzene's volatility, this category would be expected to have less release than air emissions. Also, the nitration reaction is carried out at temperatures between 55° and 90°C (Process Research, Inc., 1972).

5.3.5.3.3 Emissions Due to Disposal of Solid Residues

No data were available that permitted estimation of benzene emissions due to disposal of benzene-containing solid residues. In order to estimate these emissions, it would be necessary to know: 1) the rate

of production of benzene-containing sludges; 2) the weight % benzene in the sludge; and 3) the method of disposal of the sludge (landfill, incineration).

5.3.5.3.4 Carry-Over of Benzene into Nitrobenzene

Data were not available to permit estimation of benzene contamination in nitrobenzene. Analytical data on nitrobenzene batches would be necessary. A Level II study could pursue this area more completely.

5.3.6 Consumption of Benzene by Chlorobenzene Synthesis

5.3.6.1 Processes, Production, Locations

The 1978 chlorobenzenes production accounted for 0.3% of the total U.S. benzene consumption (USITC; see also Appendix A). The three main commercial products obtained through the chlorination of benzene are monochlorobenzene, ortho-dichlorobenzene, and para-dichlorobenzene. Additional chlorination of these produces other polychlorobenzenes, e.g., 1,2,4-trichlorobenzene. Also, meta-dichlorobenzene is manufactured by the isomerization of ortho or para-dichlorobenzene.

Commercial benzene chlorination may take two forms: 1) batch process, or 2) continuous process (Arthur D. Little, Inc., 1977). These may be executed in the vapor phase for the production of monochlorobenzene as is done by Dow, Midland, Michigan; but more generally the chlorination is carried out in the liquid phase (Arthur D. Little, Inc., 1977). Figure 5.11 schematically depicts the manufacture of chlorobenzene and the representative reaction formulae.

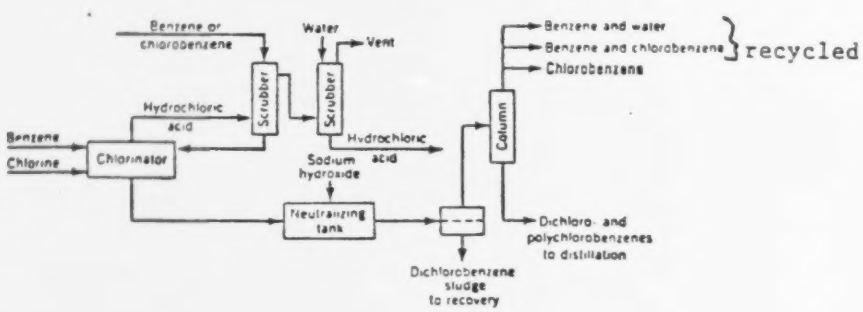
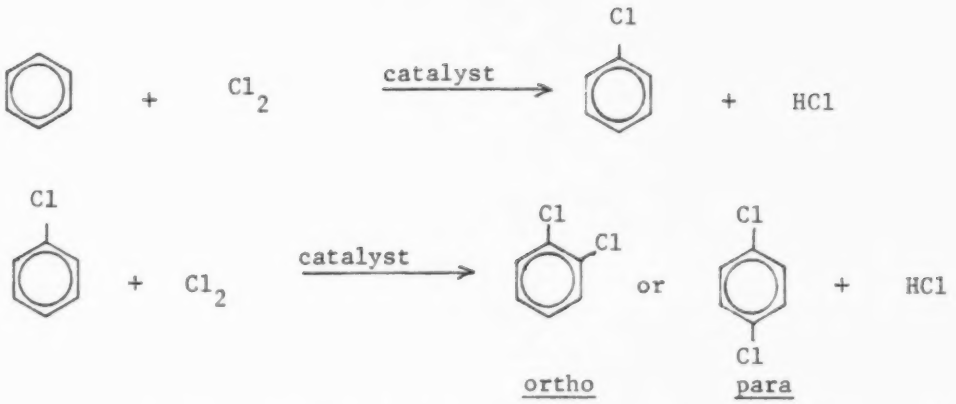


Figure 5.11 Schematic Diagram for the Production of Chlorobenzene and Dichlorobenzenes



In the batch process the benzene chlorination takes place at 40°C to 60°C in the presence of a catalyst. After the proper density is attained, the solution is neutralized, whereupon a sludge with a high dichlorobenzene content settles out and is made ready for recovery of the ortho and para structures. The balance of the neutralized solution is distilled to obtain several fractions, one of which contains 75% of the distillate and is pure monochlorobenzene (PEDCo, Inc., 1977). The residue from this distillation is the principle source of para and ortho-dichlorobenzene.

The alternate method for chlorobenzenes manufacture employs a continuous chlorination and fractionation procedure so that the monochlorobenzene is isolated as quickly as it is formed (PEDCo, Inc., 1977). At this point neutralization and distillation of the monochlorobenzene is executed in the same manner as in the batch process (PEDCo, Inc., 1977).

Figure 5.12 shows the producers of monochlorobenzene, ortho-, meta-, and para-dichlorobenzene and their locations together with their respective 1976 capacities and the corresponding benzene requirements. Independent capacity data that would assist in an assessment of the accuracy of the figures given in this table were unavailable. Furthermore, the listed capacities are subject to substantial change since the chemical processes that are involved are inherently easy to control in meeting demands for specific chlorobenzene isomers (Arthur D. Little, Inc., 1977). The full capacity benzene requirement figures were based on the following (SRI, 1977): 1) 85% yield for synthesis of the respective chlorobenzenes, 2) a conversion factor of 0.82 kkg of benzene required per

LOCATIONS

1976 CHLOROBENZENES PRODUCTION CAPACITY AND BENZENE REQUIREMENT BY COMPANIES[1]

No	Company	Location	Monochlorobenzene[2] Capacity (kkg/yr)	Dichlorobenzene Cap (kkg/yr)[3] Ortho	Meta	Para	Full Capacity Benzene[4] Requirement (kkg/yr)
1	Allied Chemical Corp., Industrial Chemicals Division	Syracuse, NY	11,000	3,600	—	5,400	14,600
2	Chemical Products Corp.	Cartersville, GA	—	10,000	—	—	6,200
3	Dow Chemical U.S.A.	Midland, MI	136,000	11,300	—	17,200	129,200
4	Eastman Kodak Co., Eastman Organic Chemicals	Rochester, NY	—	—	NA	—	NA
5	Koppers Co., In.	Follansbee, WV	NA	—	—	—	—
6	Guardian Chemical Co., Eastern Chemical Division	Hauppauge, NY	—	—	NA	—	NA
7	Dover Chemical Corp., Subsidiary of ISC Industries	Dover, OH	NA	NA	NA	NA	NA
8	Monsanto Co., Monsanto Industrial Chemicals Co.	Sauget, IL	52,000	7,300	—	5,400	30,300
9	Montrose Chemical Corp. of California	Henderson, NE	32,000	NA	—	NA	26,200[5]
10	Occidental Petroleum Corp.	Niagara Falls, NY	7,000	—	—	—	5,700
11	PPG Industries, Inc., Chemical Division	Natrium, WV	41,000	9,100	—	13,600	47,700
12	Solvent Chemical Co., Inc.	Malden, MA	NA	1,400[6]	—	NA	800[5]
13	Solvent Chemical Co., Inc.	Niagara Falls, NY	NA	9,100[7]	—	9,100[7]	5,600[5]
14	Specialty Organics, Inc.[2]	Irwindale, CA	—	1,000[8]	—	1,000[8]	600
15	Standard Chlorine Chemical Co., Inc.	Delaware City, DE	34,000	18,100[9]	—	27,200	56,000
16	Standard Chlorine Chemical Co., Inc.	Kearny, NJ	—	7,300	—	NA	5,000[5]

Figure 5.12 Chlorobenzenes from Benzene (1976)

Notes: on Figure 5.12

NA = Not Available

-- = Not Manufactured

1. Exercise care in interpreting capacities since these chemical processes can be easily altered to meet changing capacity demands.
2. From Mara and Lee, 1978, who cite SRI 1976 Directory fo Chemical Producers.
3. From Arthur D. Little, Inc., 1977 who cite SRI 1976 Directory of Chemical Producers.
4. Based on SRI, 1977 who state that 0.82 pounds of benzene are required per pound of monochlorobenzene produced, and that 0.62 pounds of benzene are required per pound of ortho- or para-dichlorobenzene produced.
5. Based on known chlorobenzenes capacities.
6. Production to be phased out.
7. Includes capacity for ortho- and para-dichlorobenzene as well as 1,2,4-trichlorobenzene.
8. Includes capacity for ortho- and para-dichlorobenzene.
9. From Arthur D. Little, Inc., 1977, who cite Chemical Profiles (o-dichlorobenzene, April 1, 1974), Schnell Publishing Company, Inc., New York.

kkg of monochlorobenzene produced, 3) a conversion factor of 0.62 kkg of benzene required per kkg of ortho- or para-dichlorobenzene produced. Although information concerning processes and capacities of commercial meta-dichlorobenzene production was limited, the companies producing this isomer are listed to indicate production locations. Benzene release would only occur if benzene chlorination took place at these facilities. The amount of the meta isomer produced was not reported and was presumably small (Arthur D. Little, 1977).

Table 5.5 lists estimated 1978, 1979 chlorobenzenes production and the corresponding benzene requirement. These data have been extrapolated from the 1976 capacity figures of Figure 5.12. It was assumed that each company produced the derivatives in a quantity that was proportional to the fraction of the total U.S. chlorobenzenes production capacity that the company supplied in 1976. Where plant capacity data were not available then the capacity was assumed to have been zero. In equation form the above is described by the following:

chlorobenzenes production of company in 1978 or 1979 = (% of total U.S. capacity for chlorobenzenes production that a company contributed in 1976) x (total U.S. chlorobenzenes production in 1978 or 1979).

Total monochlorobenzene production was taken from the U.S. International Trade Commission January to August, 1979 supplement. A total 1979 monochlorobenzene production was calculated by assuming that the production from January through August equals two-thirds of that which will be complete by the end of December. Total 1979 monochlorobenzene production was projected to be 137,000 kkg. Since 1979 ortho- and para-dichlorobenzene production data were unavailable, 1978 figures were taken from USITC: 19,000 kkg for both o- and p-dichlorobenzene. According to USITC information, several plants that were listed as having capacity for production of chlorobenzenes in 1976 did not produce these in recent years and therefore are not included in the production table nor in the calculations involved for the generation of this table.

5.3.6.2 Benzene Emissions

5.3.6.2.1 Emissions to Air

The chlorination stage in the chlorobenzenes manufacture was

Table 5.5 Estimated Chlorobenzenes Production and Benzene Requirement by Companies[1]

No	Company	Location	1979 Monochlorobenzene Production (kkg/yr)	1978 Dichlorobenzene Prod(kkg/yr) Ortho	Meta	Para	Benzene Requirement (kkg/yr)
1	Allied Chemical Corp. Industrial Chemicals Division	Syracuse, NY	4,900	1,200	--	1,600	5,800
2	Dow Chemical U.S.A.	Midland, MI	61,000	3,700	--	5,100	55,500
3	Dover Chemical Corp., Subsidiary of ICC Industries	Dover, OH	--	--	--	NA	NA
4	Monsanto Co., Monsanto Industrial Chemicals Co.	Sauget, IL	23,300	2,400	--	--	20,600
5	Montrose Chemical Corp. of California	Henderson, NE	14,300	NA	--	NA	11,800[2]
6	PPG Industries, Inc., Chemical Division	Natrium, WV	18,400	3,000	--	4,000	19,400
7	Standard Chlorine Chemical Co., Inc.	Delaware City, DE	15,200	6,000	--	8,012	21,200
8	Standard Chlorine Chemical Co., Inc.	Kearny, NJ	--	2,400	--	NA	1,500[2]

Notes:

NA = Not Available
-- = Not Manufactured

1. Exercise care in interpreting chlorobenzenes production since these chemical processes can be easily altered to meet changing demands. Figure 5.12 and USITC data have been used to calculate production by plant.

2. Based on known chlorobenzenes production.

presumably the principle source of atmospheric benzene emissions (PEDCo, 1977). Benzene emissions from the production of monochlorobenzene, o- and p-dichlorobenzene will be quantitatively discussed in this section. While m-dichlorobenzene is also a benzene derivative, the isomerization of o- or p-dichlorobenzene required for its production is not a source of benzene emissions unless the o- and p- isomers contain benzene as an impurity. However, benzene emissions were associated with m-dichlorobenzene production when one considers the emissions occurring in the synthesis of the o- or p-dichlorobenzene, the required intermediate. These emissions could not be quantified since neither the amount of o- or p-dichlorobenzene used as the intermediate nor the actual production volume of the meta structure was known. PEDCo (1977) listed the total 1975 atmospheric benzene emissions attributable to monochlorobenzene, para-dichlorobenzene and ortho-dichlorobenzene production to have been 1065, 692, and 529 kkg respectively.

The U.S. International Trade Commission lists monochlorobenzene, para-dichlorobenzene, and ortho-dichlorobenzene 1975 production to have been 138,789, 24,798 and 20,751 kkg, respectively. The emission/production quotient for each chlorobenzene isomer yielded the emission factor. These are listed in Table 5.6. PEDCo (1977) also calculated emission factors by computing the emission/production quotient. These are included in Table 5.6. They employed the same 1975 emission quantities as above. However, in order to estimate actual chlorobenzenes production they cited 1977 plant capacity data and assumed that the facilities operated at 80% of capacity.

The emission factors were applied to total U.S. production obtained from USITC to derive total atmospheric benzene emissions due to the production of each of the chlorobenzenes. USITC total production data for monochlorobenzene from January to August, 1979 were available and extrapolated to represent the entire year's production. The extrapolation assumed that production from January through August equals two-thirds of that which will be complete by December. Total 1979 monochlorobenzene production was projected to be 137,000 kkg. Since 1979 production figures for dichlorobenzenes were not accessible, total production of

Table 5.6 Benzene Emission Factors (kkg of Benzene Emitted per kkg of chlorobenzene produced)

Benzene Derivative	Emission Factors, kkg/kkg	
Monochlorobenzene	0.0077	.0035[1]
ortho-dichlorobenzene	0.0279	.0100[1]
para-dichlorobenzene	0.0255	.0072[1]

1. Source: PEDCo (1977)

Table 5.7 Benzene Emissions Due to Chlorobenzenes Manufacture

Benzene Derivative	Benzene Emissions, kkg	
Monochlorobenzene[2]	1050	480[1]
ortho-dichlorobenzene[3]	530	190[1]
para-dichlorobenzene[3]	480	140[1]

1. Based on PEDCo (1977) emission factor.
2. Based on 1979 production.
3. Based on 1978 production.

these was taken from USITC 1978, 19,000 kkg for both o- and p-dichlorobenzene.

When presenting benzene emissions due to chlorobenzenes synthesis the higher of the two estimates will be quoted in order to represent a worst-case estimate. See Table 5.7.

5.3.6.2.2 Benzene Emission to Water

Information needed to quantitatively assess benzene emissions was not available. Versar (1979) estimated that discharges to POTW from the manufacture of monochlorobenzene may be significant.

5.3.6.2.3 Benzene Emission to Land

Neither qualitative nor quantitative data concerning benzene emissions to land as a result of chlorobenzenes manufacture were available.

5.3.6.2.4 Benzene Residue in Chlorobenzenes

Inherent in the processes used to manufacture chlorobenzenes is the possibility that these are contaminated with benzene residues. Benzene emissions as a result of this phenomenon currently cannot be quantified due to the lack of relevant information.

5.3.7 Consumption of Benzene for Alkylbenzenes Synthesis

5.3.7.1 Processes, Producers, and Locations

Alkylbenzenes (also called detergent alkylates and dodecylbenzenes) are formed by the alkylation of benzene with long-chain hydrocarbons. Use of dodecene as the alkylating agent yields branched chain dodecylbenzenes, while Friedel-Crafts alkylation with n-alkylchlorides yields linear alkylbenzenes with 10-14 carbon chains (A.D. Little, Inc., 1977).

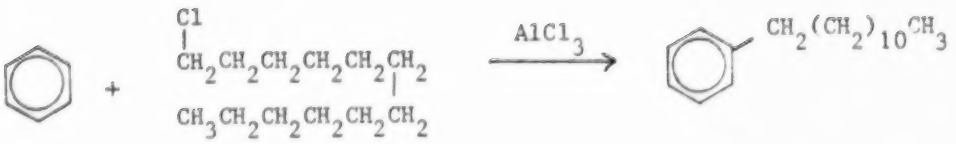
PRODUCERS AND BENZENE REQUIREMENTS[1]

Map No.	Company	Location	Benzene Requirement, 1978[2] kkg
1	Continental Oil	Baltimore, MD	29,000 (straight chain)
1	Continental Oil	Baltimore, MD	3,800 (branched chain)
2	Monsanto C.	Chocolate Bayou, TX	34,000 (straight chain)
3	Standard Oil (Chevron)	Richmond, CA	34,000 (branched chain)
4	Union Carbide	South Charleston, WV	23,000 (straight chain)
5	Witco Chem.	Carson, CA	8,400 (straight chain)
		Sum	132,000

[1]Source: PEDCo, 1977.

[2]Derived from 1976 plant capacities by the procedure described in Section 5.3.7.2.

Figure 5.13 Production of Alkylbenzenes



5.3.7.2 Amount Consumed

Figure 5.13 includes the benzene requirement for each alkylbenzene producer. This amount of benzene consumed was calculated as follows:

1) 1976 full capacity benzene requirements for each plant were calculated from 1976 production capacities (PEDCo, 1977) by using the conversion factor 0.40 kkg benzene used/kkg alkylbenzene produced for both straight- and branched-chain alkylbenzenes (Neufeld et al., 1978).

2) The percent contribution made by each plant to the total 1976 full-capacity benzene requirement was calculated.

3) It was assumed that this percent contribution also described the percent contribution to true production (as opposed to capacity) in 1978 (as opposed to 1976). The percent contribution of each plant was then multiplied by the estimated 1978 benzene consumption for alkylbenzene synthesis (Figure 5.13) to yield the 1978 benzene consumption by each plant.

5.3.7.3 Emissions Due to Alkylbenzene Synthesis

PEDCo (1977) cited a report of a personal communication between EPA and Union Carbide as the source of an emission factor for benzene release from a controlled linear alkylate process: 5×10^{-4} kkg/kkg product. This was converted to units of kkg/kkg benzene consumed using the conversion factor 0.40 kkg benzene/kkg alkylbenzene:

$(5 \times 10^{-4}$ kkg/kkg) $\div$ (0.40 kkg/kkg) $= 1.3 \times 10^{-3}$ kkg benzene released per kkg benzene consumed.

No data were available on synthesis of branched alkylbenzenes. Therefore, it was assumed that the emission factor for the linear alkylbenzene also applied to the branched alkylbenzene. This was based on the chemical similarity between the two synthesis reactions.

5.3.7.3.1 Emissions to Air

Emissions to air were judged to constitute 100% of total emissions due to alkylbenzene synthesis. This judgement was based on the following: 1) The reactions are carried out at 40-60°C, where benzene would have a significant vapor pressure (A.D. Little, 1977). 2) Versar (1979) estimated water emissions to be significant. 3) PEDCo (1977) mentions the possibility of airborne emissions from incineration of light and heavy organic ends.

Application of the overall emission factor to benzene consumption for alkylbenzene synthesis yielded: (132,000 kkg) x (1.3×10^{-3} kkg/kkg benzene used) = 170 kkg benzene released to air in 1978 due to alkylbenzene synthesis. In the absence of background information, no estimate of the uncertainty of the emission factor was possible.

5.3.7.3.2 Emissions to Water

Emissions to water were judged to be negligible. See 5.3.7.3.1.

5.3.7.3.3 Emissions Due to Disposal of Solid Residues

Emissions due to solid residue disposal were included in the estimate of releases to air (5.3.7.3.1).

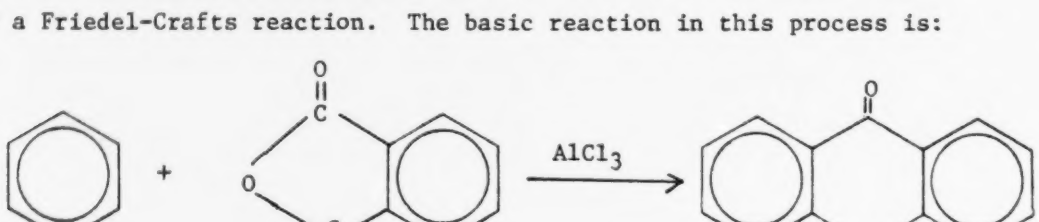
5.3.7.3.4 Carry-Over of Benzene into Product

No information was available to permit estimation of benzene contamination of alkylbenzenes. This question would be addressed in a Level II materials balance by obtaining analytical data on alkylbenzene batches.

5.3.8 Consumption of Benzene by Synthesis of Anthraquinone

5.3.8.1 Processes, Producers, Locations

According to (Merck, 1968) anthraquinone is produced from phthalic anhydride and benzene in the presence of aluminum chloride by a Friedel-Crafts reaction. The basic reaction in this process is:



Anthraquinone

The only plant listed in any literature (Fentiman et al., 1979) as producing anthraquinone is Toms River Chemical Corp., Toms River, New Jersey.

5.3.8.2 Amounts Manufactured

Neufeld et al. (1978) estimated anthraquinone production by using the USITC value for total Vat Due production. The USITC states 17,000 kkg of Vat Dye was produced in 1978. Neufeld et al. (1978) used a conversion factor of 1.37 and Vat Dye production to calculate benzene consumed for the production of anthraquinone:

(1.37) (17,000 kkg) = 23,000 kkg benzene

required for the production of anthraquinone in 1978. The uncertainty of this value was unknown.

5.3.8.3 Emissions of Benzene Due to Production of Anthraquinone

No emissions data were available with which to estimate benzene emissions due to anthraquinone synthesis. A more detailed literature search in this area might be carried out in a Level II study.

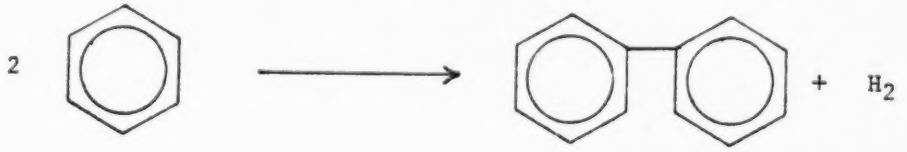
5.3.8.4 Carry-Over of Benzene into Product

Carry-over of benzene as a contaminant of anthraquinone may be a source of emissions, and should be addressed in Level II study.

5.3.9 Consumption of Benzene by Synthesis of Biphenyl

5.3.9.1 Processes, Producers, Locations

30% of the total biphenyl production is directly from benzene by the process of thermally reacting benzene vapors. (Meylan and Howard, 1976). The rest of the yearly biphenyl production does not use benzene feedstock. The basic reaction in this process is:



Biphenyl is produced from a thermal dehydrogenation of benzene shown in Figure 5.14. Benzene and the recycled benzene are vaporized, heated to about 600°C, and injected into a thermal reactor at 1-2 atm pressure. The reactor raises the temperature to 700-850°C; the time of exposure to the higher temperatures is about one second (Meylan and Howard, 1976). Biphenyl was produced by this process only at the Anniston, Alabama plant of Monsanto Industrial Chemicals Co.

5.3.9.2 Amounts Manufactured

According to USITC 29,000 kkg of biphenyl were produced in 1978. Based on the 30% figure given in Meylan and Howard (1976) for the amount of biphenyl produced from benzene:

$$(29{,}000 \text{ kkg}) \times (0.3) = 8{,}700 \text{ kkg biphenyl produced from benzene in 1978.}$$

5.3.9.3 Emissions of Benzene Due to Production of Biphenyl

Data on emissions for 1978 were not found in any available sources. Based on 1976 benzene consumption and emission data for other non-fuel uses of benzene (Versar, 1979) an emission factor was calculated to be:

$$\frac{200 \text{ kkg benzene released}}{34{,}000 \text{ kkg benzene consumed}} = 0.0059 \text{ kkg benzene emitted per kkg of benzene consumed}$$

Using the benzene conversion factor given in Meylan and Howard (1976) of 0.8 kkg benzene used/kkg biphenyl produced, benzene consumption in the production of biphenyl was:

$$\frac{8{,}700}{0.8} = 11{,}000 \text{ kkg of benzene consumed}$$

in the production of biphenyl in 1978. Based on these calculations, benzene emissions were estimated to be:

$$(11{,}000 \text{ kkg})(0.0059 \text{ kkg/kkg}) = 65 \text{ kkg benzene released due to biphenyl synthesis during 1978.}$$

Considering the uncertainties of the 1976 benzene emission value (200 kkg $\pm$ an estimated factor of 2) and the conversion factor (0.8 $\pm$ an estimated 20%) we estimated the cumulative uncertainty of the benzene emissions in 1978 to be 65 kkg $\pm$ a factor of 3.

5.3.9.3.1 Emissions to Air

Based on the calculations for emissions from Versar (1979), it was judged that 99.5% of the emissions of benzene from the production of biphenyl were to the air. Application of this percentage to total estimated emissions yielded:

(65 kkg)(0.995) = 64 kkg of benzene released to air during biphenyl synthesis.

5.3.9.3.2 Emissions to Water

As discussed in 5.3.9.3.1, it was estimated that 0.5% of total emissions were to water. Application of this value to total estimated emissions yielded:

(64 kkg)(0.005) = 0.3 kkg benzene released to water during biphenyl synthesis in 1978.

5.3.9.3.3. Emissions Due to Disposal of Solid Residues

According to Meylan and Howard (1976), the only wastes from the biphenyl process are the crude still pot residues. It is likely that a small amount of benzene will be present in these residues, however no data were available to permit estimation.

5.3.9.3.4 Carry-Over of Benzene into Product

Carry-over of benzene as a contaminant of biphenyl may be a source of emissions, and should be addressed in a Level II study.

5.3.10 Benzenesulfonic Acid

Benzenesulfonic acid is a direct consumptive use of benzene, used only in the production of phenol. According to Neufeld *et al.* (1978), Reichold Chemicals, the only company producing phenol *via*

the benzenesulfonic acid method, closed its plant in 1978. It was not possible to estimate emissions for previous years.

5.3.11 Exports of Benzene

5.3.11.1 Amount Exported

Data provided by the Bureau of the Census (personal communication) showed the following amounts exported:

1978	1979[1]
151,000	68,000

1. Extrapolated from January - October preliminary figures.

5.3.11.2 Emissions Due to Benzene Export

Emissions due to export were considered to be attributable to transport plus dockside loading. Emission factors for these processes have been estimated by PEDCo (1977), and these factors were applied to the export value (above). The results are summarized in Table 6.4. Total estimated emissions were 17 kkg.

Table 5.8 Emission Factors and Emissions Due to Benzene Export, 1978[1]

Process	Emission Factor, kkg/kkg	Emissions, kkg
Benzene transport	1.1×10^{-4}/week	17[2]
Benzene loading	6.9×10^{-8}	0.01
	Sum:	17 kkg

1. Source: PEDCo, 1977.
2. The average time in transit was estimated to be one week.

5.3.11.2.1 Emissions to Air

Of the total emissions estimated in 5.3.11.2, it was estimated that 90% were released to air and 10% to water. This was based on

the following: 1) The only significant emissions were those due to transport. 2) Most spill losses would be over land, and the benzene would evaporate before reaching water. 3) Fugitive losses would be mostly evaporation during transfers.

Application of this breakdown of total emissions yielded:

(17 kkg) (0.9 fraction to air) = 15 kkg benzene released to air due to exportation.

5.3.11.2.2 Emissions to Water

As discussed in 5.3.11.2.1, emissions to water were estimated to be:

(17 kkg) (0.1 fraction to water) = 2 kkg benzene released to water during exportation.

It was estimated that emissions to landfills or to solid residues due to export of benzene would be negligible.

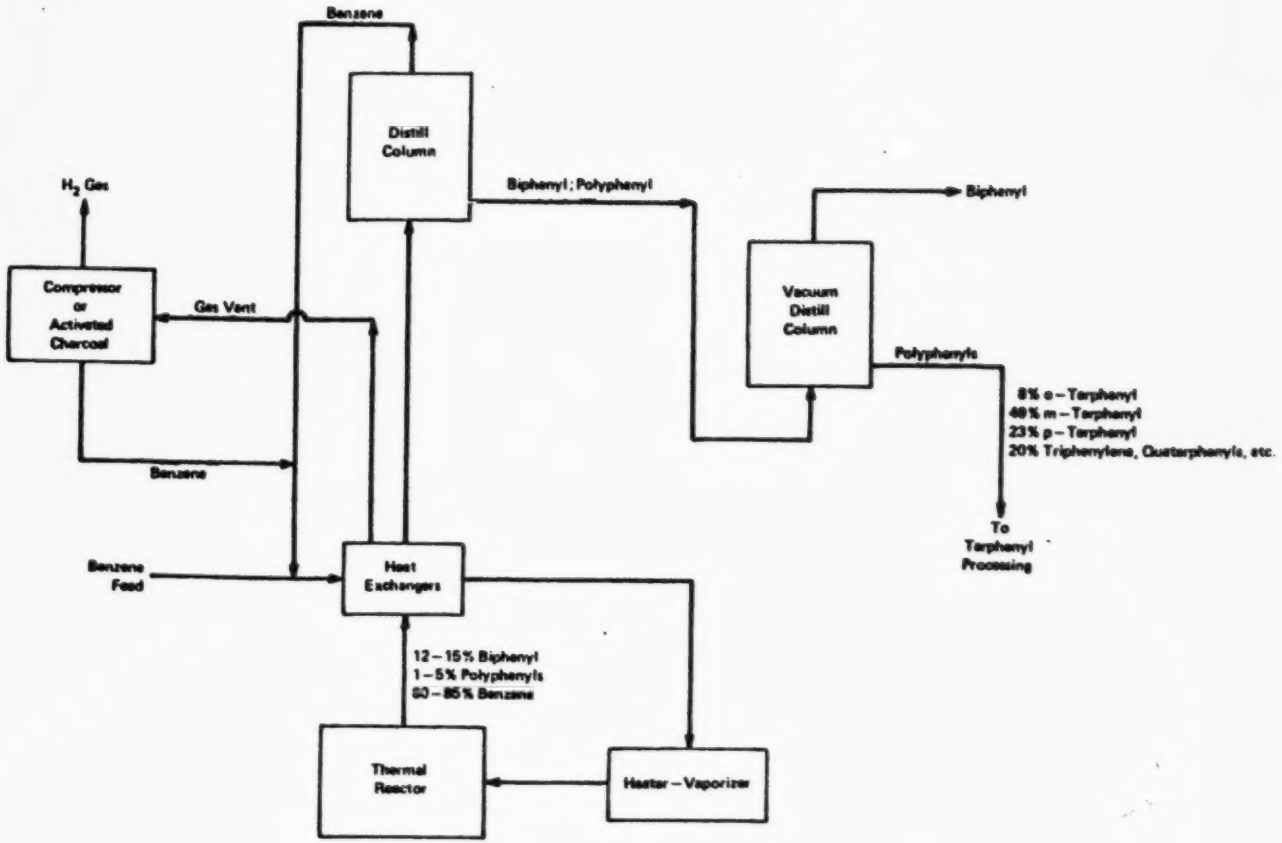


Figure 5.14 Biphenyl from Thermal Dehydrogenation of Benzene

Source: Meylan and Howard, 1976

Table 5.2 Consumptive Uses of Benzene, 1975-1979[1]

Use	Amount of Benzene Consumed, Thousands of kkg									
	1975		1976		1977		1978		1979[2]	
	kkg	%	kkg	%	kkg	%	kkg	%	kkg	%
Ethylbenzene	1,760	48	2,380	51	2,580	53	2,890	54	2,910	52
Cumene	619	17	840	18	816	17	1,058	20	1,240	22
Cyclohexane	596	16	752	16	771	16	811	15	839	15
Nitrobenzene	228	6	169	4	228	5	170	3	187[3]	3
Maleic Anhydride	115	3	137	3	120	2	161	3	172	3
Chlorobenzenes	140	4	151	3	151	3	133	2	145	3
Detergent Alkylates	122	3	131	3	131	3	132	2	157	3
Anthraquinone	26	0.7	33	0.7	33	0.7	23	0.4	n.a.	--
Biphenyl	9	0.2	9	0.2	9	0.2	11	0.2	n.a.	--
Benzenesulfonic Acid	44	1	54	1	54	1	0	0	0	0
Total	3,660	98.9	4,660	99.9	4,890	100.9	5,389	99.6	5,650	101

1. Neufeld et al., 1978.
2. Partial data from USITC were used to estimate these values.
3. Estimated by the operation: 1979 benzene consumption = $\frac{\text{1979 aniline production}}{\text{1978 aniline production}}$ x 1978 benzene consumption.

6.0 NONCONSUMPTIVE USES OF BENZENE

Nonconsumptive uses are uses in which benzene is not removed from the materials balance by chemical destruction or export. Examples are given and discussed below.

6.1 TOTAL NONCONSUMPTIVE USE

Nonconsumptive use is a minor category of benzene use. An economic input/output analysis for benzene (Neufeld et al., 1978) estimated that the categories Miscellaneous Chemical Conversions + Solvent Uses + Inventory Changes accounted for 5.1 percent of production in 1977. In the absence of independent data, the 5.1 percent contribution was applied to 1978 data:

(5,389,000 kkg benzene consumed)(0.051) = 270,000 kkg benzene used for miscellaneous chemical syntheses + solvent use + inventory change in 1978.

Assuming the 1977 percent contribution is applicable, this value represents an upper bound for nonconsumptive uses, since it also contains an unknown amount of minor consumptive uses.

6.2 CATEGORIES OF USE

There are two categories of nonconsumptive uses for benzene, as shown in Table 6.1. The amounts attributed to each category are estimates.

6.3 EMISSIONS BY CATEGORY OF USE

6.3.1 Use of Benzene as a Solvent

A small fraction of benzene production is used as a solvent in various processes. Its use in this way has been dropping since the 1977 OSHA Emergency Benzene Standard and the issuance of a regulation by the Consumer Product Safety Commission banning benzene in consumer products, according

Table 6.1 Nonconsumptive Uses of Benzene

Use	Amount (kkg), 1978
Solvent	9,500[1]; 27,000[2]
Inventory Change	-272,000
Total	270,000[3]

1. Source: Estimate by Neufeld et al., 1978.
2. Source: Mara and Lee, 1978.
3. Maximum value, estimated independently in section 6.1; not the sum of uses.

to Neufeld et al. (1978). This statement was based on interviews with 405 companies that used benzene as a solvent in either chemical manufacturing processes or in consumer goods.

6.3.1.1 Locations of Use

Analysis of benzene sales for solvent use in 1976 revealed the following geographical distribution (Neufeld et al., 1978):

Region	States	Percent of Total Benzene Solvent Use
West South Central	TX, LA, AR, OK	51
Middle Atlantic	NY, PA, NJ	31
East North Central	WI, IL, IN, MI, OH	10
East South Central	KY, TN, MS, AL	5
West North Central	ND, SD, NB, KS, MN, IA, MO	1

6.3.1.2 Amounts of Use

Two estimates of the amount of benzene used as a solvent are presented in Table 6.1. The value 9,500 kkg was estimated by Neufeld et al. (1978) by summing projections of 1978 usage. These projections would have been complicated by the OSHA and CPSC actions of 1977, and the uncertainty of the estimate is approximately +10 percent, -50 percent.

The second estimate (Mara and Lee, 1978) is based on estimates of the fraction of total benzene production that is used nonconsumptively. Their estimate of 27,000 kkg used as solvents would have an estimated uncertainty of ±80 percent.

In the absence of a sound method to select between the values, the higher estimate was selected in order to give a worst-case estimate of emissions.

6.3.1.3 Emissions Due to Solvent Use

Neufeld et al. (1978) have recently reported on use of benzene as a solvent and the emissions associated with this use. Table 6.2 summarizes their estimates. These authors also document the effect

Table 6.2 Estimated Emissions of Benzene as a Solvent[1]

Type of Solvent Use[2]	Estimated Emissions, kkg, 1978
General Organic Synthesis	1,000
Pharmaceutical Synthesis	200
Small Volume Chemicals	
Aluminum Alkyls	1,000
Alcohols	200
Paint Removers	500[3]
Sum:	2,900

1. Source: Neufeld et al., 1978. Estimates of emissions were based on emission control information obtained during interviews with companies using benzene as a solvent.
2. Other types of use that either no longer employed benzene or produced an estimated zero emissions of benzene were: Bisphenol-A, ethyl cellulose, adhesives, tire manufacture, tire retreading, industrial rubber products, tire patch repair kits, automotive adhesives, shoe adhesives, paints and coatings.
3. Due to product manufactured before May, 1977, and sold in 1978.

of the 1977 OSHA and CPSC actions on benzene use: Estimated losses of benzene due to solvent use were 6,000 - 7,000 kkg in 1976 and 2,900 kkg in 1978. Cyclohexane is replacing benzene in many solvent uses.

6.3.1.3.1 Emissions to Air

Distribution of the total emissions among air, landfill, and water required estimation. On the average, 50 percent of emissions were estimated to be airborne and 50 percent waterborne. This estimate was based on the observations that: 1) Chemical manufacturing is more likely to cause releases to water, due to the nature of the synthesis processes, and 2) Formulation uses are more likely to yield uncontrolled evaporation.

Based on this reasoning, the estimated emissions to air were: (2,900 kkg) x (0.5) = 1,450 kkg benzene released to air during use as a solvent in 1978.

6.3.1.3.2 Emissions to Water

Based on the reasoning in 6.3.1.3.1, the emissions to water would be 1,450 kkg benzene released during solvent use in 1978.

6.3.1.3.3 Emission Due to Disposal of Solid Residues

Releases of benzene due to disposal of solid residues were not quantifiable but were estimated to be small. In order to evaluate these emissions, it would be necessary to know: 1) the rate of production of benzene-containing residues, 2) the weight % benzene in the residues, and 3) the method of residue disposal.

6.3.1.3.4 Carryover of Benzene into Products

Benzene may be carried over into products during use as a solvent in chemical synthesis. This area should be addressed in Level II study.

6.3.2 Changes in Benzene Inventory

Changes in the inventory of benzene during a given year may be considered "negative" or "positive" nonconsumptive use. Emissions due

to inventory have been considered under storage emissions. The purpose of the present estimate of inventory change is to aid in balancing supplies with uses.

The December 31 inventories of benzene for 1977 and 1978 are shown below. During 1978, inventories dropped by 272,000 kkg.

Year	Benzene Inventory as of 21/31, kkg	Change During 1978
1977	643,000[1]	
		-272,000 kkg
1978	371,000[2]	

1. Source: National Petroleum Refiners Association, as cited in Neufeld et al., 1978.

2. Source: National Petroleum Refiners Association (personal communication with Linda Dziuban).

7.0 USE OF BENZENE AS A FUEL COMPONENT

7.1 BENZENE IN GASOLINE

7.1.1 Concentration of Benzene in Gasoline

The benzene concentration in gasoline depends on several factors including the source of the crude oil from which the gasoline was made, the geographical location of the source and the refiner, the grade of gasoline, refinery operations, and the seasonal blends produced by each refinery (PEDCo, 1977).

Prior to 1974, the average benzene content in U.S. gasoline was less than 1 percent by volume. More recent data indicate that the average benzene content has been increased to maintain octane levels as lead content has been reduced (Mara and Lee, 1978). A NIOSH study using 1976 data found an average benzene concentration of 1.24 percent by liquid volume (a weighted average based on fuel type and amounts produced). A nationwide survey during February and March 1977 produced a range of concentration from 1.25 to 5.0 percent, averaging out to 2.5 percent benzene by volume. This value might be high since benzene concentrations are greater in winter blends. The investigators in this survey estimated an average of 2 percent throughout the year (PEDCo, 1977). In the present report, we will assume a value of 2 percent by liquid volume for benzene concentration in gasoline during 1979.

7.1.2 Amount of Benzene in Gasoline

The 1979 consumption of gasoline was estimated to be 1.08×10^{11} gallons (American Petroleum Institute, 1980). We judge the uncertainty of this value to be ± 10 percent. The 1979 benzene content of gasoline totaled:

$$(1.08 \times 10^{11} \text{ gal})(2\%) = 2 \times 10^{9} \text{ gal benzene} = 7 \times 10^{6} \text{ kkg benzene.}$$

Since this is larger than the annual production of benzene, it is probably more accurate to consider benzene as a native constituent of

gasoline rather than an additive. It is unknown how much of this benzene originates in the 4,960,000 kkg of direct benzene production, but is unlikely that a significant amount does. The basis for this statement is the fact that aromatics (including benzene) for gasoline are contained in reformate which makes up 20 percent of the "pool" of materials going into gasoline. BTX (a mixture of benzene, toluene, and xylene) is often separated from reformate and then is blended back into the gasoline pool along with other octane-raising compounds (USITC, 1978). Thus, if benzene is used as an octane-raising additive, it is mixed in the gasoline pool as a component of BTX and not as pure benzene. In this situation the benzene would not be counted in total benzene production reports since it was not separated from the BTX. Gasoline production, therefore, significantly contributes to the amount of benzene made available to the environment, and gasoline usage thus becomes a potentially great source of benzene emissions.

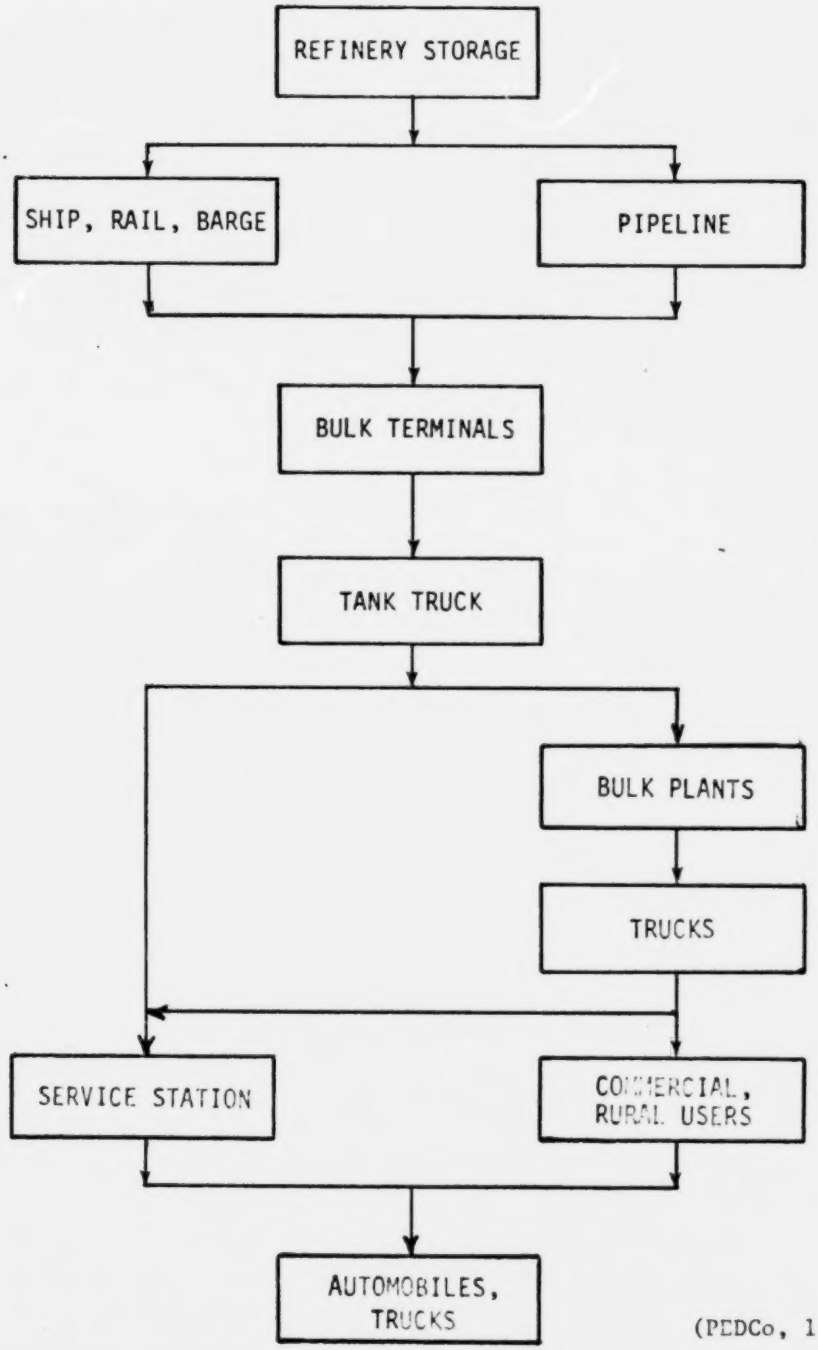
7.1.3 Benzene Emissions from Gasoline Use

7.1.3.1 Benzene Emissions Due to Gasoline Production

No factors for benzene emissions to air, land or water specifically attributable to the production of gasoline were found in the literature. Since gasoline is produced at refineries where presumably other processes are also taking place, any emissions from gasoline production specifically would be included in emissions from petroleum refineries generally. See Section 3.1 for emissions from petroleum refineries in general.

7.1.3.2 Benzene Emissions Due to Gasoline Storage

Figure 7.1 is a diagram representing the flow of gasoline from production center to its ultimate combustion in a motor vehicle engine. The gasoline distribution system involving transport from the petroleum refineries to the consumer, with intermediate storage stops, may be a significant source of atmospheric benzene. Gasoline is shipped from refinery storage areas to bulk terminals (regional distribution centers) by ship, barge, railcar, and pipeline. It is then transported from the



(PEDCo, 1977)

Figure 7.1 Gasoline Distribution System

terminal by tank truck to service stations and commercial and rural users, either directly or via bulk plants (local distribution centers) (PEDCo, 1977; Mara and Lee, 1978).

Gasoline may be stored in either floating-roof or fixed-roof tanks, each with its own emission characteristics. Floating-roof tanks are more common to refineries and very large storage sites. They do not emit the "breathing" emissions associated with fixed-roof tanks (JRB, 1980). We have assumed that all the gasoline produced is stored in floating-roof tanks at bulk terminals, since it is not known exactly how many terminals have floating-roof tanks. Emissions from refinery storage are covered in the section on refinery emissions.

Hydrocarbon emissions from floating-roof tanks occur primarily from standing and withdrawal losses. Standing losses are caused by the improper fit of the seal and shoe to the vessel shell and when vapor escapes between the flexible membrane seal and roof. Withdrawal losses are caused by evaporation of gasoline from the tank walls as the roof descends during emptying operations (Mara and Lee, 1978). In this report, we have used PEDCo's methods of calculating emissions from floating-roof tanks since their explanation of the process appeared more complete.

Method of calculation (from PEDCo, 1977):

1. Assume that all gasoline is stored in floating-roof tanks with a typical capacity of 2.3×10^6 gal (8,700 m^3).
2. Assume that the average tank retention time is 30 days.
3. Assume that the average tank is 75 percent full.
4. Use the following factors for hydrocarbon losses:
   a. 132 lb/day/tank for standing storage losses.
   b. 0.025 lb/10^3 gallons for losses during withdrawal.
5. Apply these factors to the Annual Domestic Gasoline Consumption (ADGC) in gallons to get total hydrocarbon emissions.

6. To convert hydrocarbon emissions to benzene emissions assume benzene to be equal to 2 percent by liquid volume of gasoline and vapor-phase concentration at 40 percent of liquid concentration (converted to vapor weight basis, this is 45 percent).

We have used 1.08×10^{11} gallons from Section 7.1.2 as the 1979 ADGC. Benzene emissions to air from standing storage of gasoline in floating-roof tanks equal:

$$\frac{(1.08 \times 10^{11}\text{gal})(132 \frac{\text{lb}}{\text{day} \cdot \text{tank}})(30 \text{ days})(0.02)(0.45)(454 \times 10^{-6} \frac{\text{kkg}}{\text{lb}})}{(2.3 \times 10^{6} \frac{\text{gal}}{\text{tank}})(0.75 \text{ full})}$$

= 1,000 kkg benzene emitted to air during standing storage in 1979.

Because the uncertainty of the emission factor was not discussed in the literature available, an uncertainty could not be assigned to this emission estimate. Benzene emissions to air from withdrawal of gasoline from floating-roof tanks equal:

$$(1.08 \times 10^{11}\text{gal})(0.025 \frac{\text{lb}}{10^{3}\text{gal}})(0.02)(0.45)(454 \times 10^{-6} \frac{\text{kkg}}{\text{lb}}) =$$

10 kkg benzene emitted to air during withdrawal in 1979.

It was not possible to evaluate the uncertainty range of this value.

There was no indication in the literature of emissions due to the filling of these tanks, thus none were calculated.

Gasoline bulk plants (centers for local distribution of gasoline) contain a large number of fixed-roof gasoline tanks (JRB, 1980). These plants handle a low volume of gasoline---approximately 4,000 gallons per day (uncertainty: $\pm$ 25 percent)---as opposed to the 250,000 gallons per day for bulk terminals (Mara and Lee, 1978).

The 1972 Census of Business indicated that there were 23,367 bulk plants in the United States. The number is believed to be decreasing. The number of plants dropped 11 percent between 1967 and 1972. Assuming that the number of plants continued to decrease at approximately the same rate (2.2 percent per year, or about 15 percent between 1972 and 1979), there were about 20,000 ($\pm$ 20 percent) such plants in operation in 1979

(JRB, 1980). Using these values, the volume of gasoline passing through bulk plants in 1979 was estimated to be:

$$(4{,}000 \text{ gal/plant/day})(365 \text{ days})(20{,}000 \text{ plants}) = 3 \times 10^{10} \text{ gallons.}$$

This was about one quarter of the total U.S. annual consumption. The uncertainty of this estimate was judged to be $\pm$ 50 percent.

Thirty percent of the bulk terminals are underground storage facilities, and thus do not use fixed-roof tanks. The typical gasoline bulk plant contains three tanks. An above-ground fixed-roof tank is estimated to lose 3 kg/day of gasoline vapors to breathing losses (caused by diurnal temperature changes causing expansion of the material in the tank with resultant vapor escape through vents to air)(JRB, 1980). Based on the above, we estimated the hydrocarbon emissions to air from tank breathing to be:

$$\begin{bmatrix}20{,}000\\ \text{plants}\end{bmatrix}\begin{bmatrix}70\%\ \text{above-}\\ \text{ground}\\ \text{facilities}\end{bmatrix}\begin{bmatrix}3\ \text{tanks/}\\ \text{plant}\end{bmatrix}\begin{bmatrix}3 \times 10^{-3}\ \text{kkg/}\\ \text{day/tank}\\ \text{loss}\end{bmatrix}\begin{bmatrix}365\\ \text{days/}\\ \text{year}\end{bmatrix} = \begin{matrix}5 \times 10^{4}\ \text{kkg}\\ \text{hydrocarbon}\\ \text{emissions}\end{matrix}$$

This is converted to benzene emissions by using the 2 percent benzene in gasoline by liquid volume factor and 0.45 vapor-phase conversion factor (PEDCo, 1977):

$$(5 \times 10^{4} \text{ kkg/1 yr})(0.02)(0.45) = 500 \text{ kkg/yr benzene lost to air from tank breathing}$$

The uncertainty of this value could not be estimated because the origin and reliability of the emission factor were unknown.

Fixed-roof tanks also emit hydrocarbon vapors while they are being filled. The liquid gasoline will displace an equal volume of vapor and force it into the atmosphere. Filling operations emissions can be controlled by vapor balance systems, hydrocarbon oxidation systems, and refrigerated vent systems. These emission control systems typically reduce tank filling losses and emissions by approximately 80 percent. We assumed that 25 percent of fixed-roof tanks have emission controls (JRB, 1980).

Benzene emissions due to filling of fixed-roof tanks were estimated using the following assumptions and steps:

1. $(3 \times 10^{10}$ gal stored/yr)(70% in above-ground fixed-roof tanks) = 2×10^{10} gal stored in above-ground fixed-roof tanks.

2. There will be 2×10^{10} gal of vapor vented in 1 year (or 8×10^{10} ℓ).

3. Assume this gasoline vapor is at 1 atm pressure.

4. The volume of benzene in the vapor =

$$(8 \times 10^{10}\ \ell)\begin{bmatrix}0.02 \text{ fraction} \\ \text{of benzene in} \\ \text{gasoline}\end{bmatrix}\begin{bmatrix}0.40 \text{ conversion} \\ \text{of benzene liquid} \\ \text{to benzene vapor}\end{bmatrix} = \begin{matrix}6 \times 10^{8}\ \ell \\ \text{benzene vapor} \\ \text{displaced.}\end{matrix}$$

5. Assume standard temperature and pressure (25°C, 1 atm); then-

$$\frac{22.4\ \ell}{78\ g} = \frac{6 \times 10^{8}\ \ell}{X\ g},\quad X = (6 \times 10^{8}\ \ell)\left(\frac{78}{22.4\ \ell}\right) = 2 \times 10^{9}\ g =$$

2,000 kkg displaced (uncontrolled).

6. Assuming 25 percent of these emissions are controlled (500 kkg), and that the controlled emissions are reduced by 80 percent (or 400 kkg), the total benzene emissions from filling above-ground fixed-roof tanks = 2,000 - 400 = 1,600 kkg. We estimate the uncertainty of this value as $\pm$ a factor of 4, based on the values entering into the total.

No information on emissions to air from fixed-roof tanks during gasoline withdrawal was found in the literature, therefore none were calculated. We believe such emissions to be unlikely, since fresh air would be drawn into the tanks during gasoline withdrawal, rather than hydrocarbon vapor being pushed out.

As mentioned earlier, 30 percent of the bulk plants are underground facilities (JRB, 1980). We assumed, therefore, that $(0.30)(3 \times 10^{10}$ or 1×10^{10} gallons of gasoline were stored in such facilities. No information on such facilities was found in the literature, though it would be reasonable to assume that underground storage tanks are of fixed volume and would be subject to the same type of filling "displacement" emissions as above-ground fixed-roof tanks are. Assuming no controls, and making the same assumptions and calculations as done above for above-ground fixed-roof tanks (but for half the volume), we estimated

that 1,000 kkg of benzene were emitted from underground tanks during filling. This estimate has a probable uncertainty of ± a factor of 4.

As with above-ground fixed-roof tanks, it would be reasonable to assume that gasoline withdrawal from underground tanks causes negligible emissions. There is, however, the possibility of standing storage loss from underground tanks---either "breathing" losses or losses specific to that type tank. We encountered no information in the literature on such losses and, therefore, made no estimates. This is an area which should be considered in a Level II or III report.

No factors for emissions of benzene to water or land during gasoline storage operations were found in the literature, thus no emissions were calculated. Due to the high volatility of benzene, it is believed that such emissions, if any, would be negligible.

Total benzene emissions to air from gasoline storage at bulk terminals and plants were estimated to be 1,000 kkg (floating-roof) + 10 kkg (withdrawal from floating-roof) + 500 kkg (fixed-roof, breathing) + 1,600 kkg (fixed-roof, filling) + 1,000 kkg (underground filling) = 4,000 kkg plus underground storage losses. It was not possible to assign an overall uncertainty to this estimate.

7.1.3.3 Benzene Emissions Due to Gasoline Transportation

As can be seen from Figure 7.1, presented earlier, there are several points on the gasoline flow diagram at which the product is loaded into a conveyance of some type and shipped to a distribution center. No data were available on amounts transported by pipeline, ship, rail, or barge. It appears that all gasoline is transported by truck eventually in order to get to the service stations and commercial and rural users. Transit times, however, are unknown, and probably vary depending upon each region's and locality's transportation and distribution system. Several assumptions were made in order to estimate emissions from transportation of gasoline. These assumptions were unsupported by direct data. The data should be developed as part of a Level II or Level III materials balance.

We assumed the following:

1. All the gasoline produced leaves the refinery storage area by railcar or marine conveyance (ship or barge), since we have no data whatsoever on pipeline transport.

2. Fifty percent of the gasoline is transported by railcar and 50 percent by marine conveyance between the refinery and bulk terminal; and all transport between terminal, bulk plant and service stations is by truck.

3. Seventy-five percent of the tank cars are filled by the submerged-filling or bottom-loading methods (gasoline being charged to the vehicle below the liquid surface) and 25 percent by the splash-filling method (involving a "freefall" of gasoline through the air)(PEDCo, 1977).

4. An overall efficiency of 95 percent was assumed for vapor recovery/containment for loading and unloading of rail tank-cars and tank-trucks, and unloading of barges and ships (PEDCo, 1977).

5. Gasoline has an average benzene content of 2 percent by liquid volume; the conversion factor for benzene liquid volume to benzene vapor weight is 0.45 (PEDCo, 1977).

6. The following emission factors were used (PEDCo, 1977):

Emission Source	Uncontrolled Hydrocarbon Emission Factor
Loading:	
Tank car/Truck-Splash	12 lb/10^3 gal
Tank car/Truck-Submerged	5 lb/10^3 gal
Marine	1.8 lb/10^3 gal
Transit	3 lb/wk/10^3 gal
Unloading	2.1 lb/10^3 gal

7. Transit time between the refinery and bulk terminal was assumed to be one week; bulk terminal to service station or bulk plant was one day; and bulk plant to service station and/or commercial-rural users was one day.

8. The annual domestic gasoline consumption was 1.08×10^{11} gallons (see Section 7.1.2).

9. The amount of gasoline handled by bulk plants was 3×10^{10} gallons (see Section 7.1.3.2).

Benzene emissions due to transport of gasoline from refinery storage to bulk terminal were estimated as follows:

Loading tank cars, splash method:

$(1.08 \times 10^{11}$ gal)(0.50 to tank cars)(0.25 splash method) x (12 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled emissions)(0.02 benzene in gasoline)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 30 kkg.

Loading tank cars, submerged method:

$(1.08 \times 10^{11}$ gal)(0.50 to tank cars)(0.75 submerged method) x (5 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled emissions)(0.02 benzene in gasoline)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 40 kkg.

Loading marine conveyances:

$(1.08 \times 10^{11}$ gal)(0.50 to marine)(1.8 lb/10^3 gal hydrocarbon emission factor)(0.02 benzene in gasoline)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 400 kkg.

Transit (all modes):

$(1.08 \times 10^{11}$ gal)(3 lb/wk/10^3 gal)(1 week transit time) x (0.02 benzene in gasoline)(0.45 vapor phase conversion) x $(454 \times 10^{-6}$ kkg/lb) = 1,000 kkg.

Unloading (all modes):

$(1.08 \times 10^{11}$ gal)(2.1 lb/10^3 gal)(0.05 uncontrolled emissions) (0.02 benzene in gasoline)(0.45 vapor phase conversion) $(454 \times 10^{-6}$ kkg/lb) = 50 kkg.

Total benzene emissions, transport of gasoline from refinery to bulk terminal = 30 kkg + 40 kkg + 400 kkg + 1,000 kkg + 50 kkg = 2,000 kkg.

Emissions due to transport of gasoline by tank truck from bulk terminal to service stations and bulk plants were calculated as follows:

Loading tank truck, splash method:

$(1.08 \times 10^{11}$ gal)(0.25 splash method)(12 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled)(0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 70 kkg.

Loading tank truck, submerged method:

$(1.08 \times 10^{11}$ gal)(0.75 submerged method)(5 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled)(0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 80 kkg.

Transit:

$(1.08 \times 10^{11}$ gal)(3 lb/wk/10^3 gal)(1/7 week in transit) x (0.02 benzene in gasoline)(0.45 vapor phase conversion) x (454 x 10^{-6} kkg/lb) = 200 kkg.

Unloading:

$(1.08 \times 10^{11}$ gal)(2.1 lb/10^3 gal)(0.05 uncontrolled emissions)(0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 50 kkg.

Total benzene emissions, transport of gasoline from bulk terminals to service stations and bulk plants = 70 kkg + 80 kkg + 200 kkg + 50 kkg = 400 kkg.

Benzene emissions due to transport of gasoline from bulk plants to commercial-rural users and service stations were calculated as follows:

Loading tank truck, splash method:

$(3 \times 10^{10}$ gal thru plants)(0.25 splash method)(12 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled)(0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 20 kkg.

Loading tank truck, submerged method:

$(3 \times 10^{10}$ gal thru plants)(0.75 submerged method)(5 lb/10^3 gal hydrocarbon emission factor)(0.05 uncontrolled) (0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 20 kkg.

Transit:

$(3 \times 10^{10}$ gal thru plants)(3 lb/wk/10^3 gal)(1/7 week in transit) (0.02 benzene in gasoline)(0.45 vapor phase conversion) (454 x 10^{-6} kkg/lb) = 50 kkg.

Unloading:

$(3 \times 10^{10}$ gal thru plants)(2.1 lb/10^3 gal)(0.05 uncontrolled emissions)(0.02 benzene in gasoline)(0.45 vapor phase conversion)(454 x 10^{-6} kkg/lb) = 10 kkg.

Total benzene emission from transport of gasoline from bulk plants to commercial-rural users and service stations = 20 kkg + 20 kkg + 50 kkg + 10 kkg = 100 kkg. Total benzene emissions due to transportation of gasoline = 2,000 kkg (refinery to bulk terminal) + 400 kkg (bulk terminal to bulk plants and service stations) + 100 kkg (bulk plants to service stations, etc.) = 3,000 kkg. It was not possible to assign an uncertainty to this sum due to a lack of information on the emission factors contained in the individual terms.

7.1.3.4 Benzene Emissions Due to Gasoline Vending

We assumed that commercial and rural users have the same types of storage and dispensing facilities, and therefore the same emission characteristics, as service stations. This assumption allowed us to consider the national gasoline consumption volume as having passed through service stations.

There are several sources of benzene emissions at service stations. Emissions occur from the displacement of hydrocarbon vapors to the atmosphere while gasoline is being loaded into storage tanks, from underground tanks breathing, and from vehicle refueling operations (PEDCo, 1977).

The estimates of benzene emissions from service stations were based on the rate of gasoline consumption (from Section 7.1.2), a 2 percent benzene content by liquid volume, and a 0.45 factor used to convert liquid concentration (volume percent) to vapor concentration (weight percent). The emission factors and estimated frequencies of usage from PEDCo (1977) are summarized below.

Emission Source	Hydrocarbon Emission Rate, lb/10^3 gal	Relative Frequency of Use, %
Filling Storage Tank:		
Submerged	7.3	50
Splash	11.5	25
Balanced	0.3	25
Underground Tank Breathing	1.0	100
Vehicle Refueling Displacement Losses		
Uncontrolled	9.0	75
Controlled	0.9	25
Spillage (all assumed to evaporate)	0.7	100

Emissions due to the individual processes listed in the table are estimated below.

Filling storage tanks, submerged:

$(1.08 \times 10^{11}$ gal)(0.50 usage)(7.3 lb/10^3 gal submerged emission rate)(0.02 benzene) x (0.45 vapor phase conversion) $(454 \times 10^{-6}$ kkg/lb) = 2,000 kkg from submerged filling.

Filling storage tanks, splash:

$(1.08 \times 10^{11}$ gal)(0.25 usage)(11.5 lb/10^3 gal splash emission rate)(0.02 benzene)(0.45 vapor phase conversion) $(454 \times 10^{-6}$ kkg/lb) = 1,000 kkg from splash filling.

Filling storage tanks, balanced:

$(1.08 \times 10^{11}$ gal)(0.25 usage)(0.3 lb/10^3 gal balanced emission rate)(0.02 benzene)(0.45 vapor phase conversion) $(454 \times 10^{-6}$ kkg/lb) = 30 kkg from balanced filling.

Total filling emissions: 3,000 kkg.

Underground tank breathing:

$(1.08 \times 10^{11}$ gal)(1.0 lb/10^3 gal emission factor)(0.02 benzene)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 400 kkg from underground tank breathing.

Vehicle refueling displacement losses, uncontrolled:

$(1.08 \times 10^{11}$ gal)(0.75 usage)(9 lb/10^3 gal uncontrolled emission factor) x (0.02 benzene)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 3,000 kkg from uncontrolled refueling.

Vehicle refueling displacement losses, controlled:

$(1.08 \times 10^{11}$ gal)(0.25 usage)(0.9 lb/10^3 gal controlled emission factor)(0.02 benzene)(0.45 vapor phase conversion)$(454 \times 10^{-6}$ kkg/lb) = 100 kkg from controlled refueling.

Total vehicle refueling emissions: 3,000 kkg.

Spillage emissions:

$(1.08 \times 10^{11}$ gal)(0.7 lb/10^3 gal emission factor)(0.02 benzene)(1 total evaporation) x $(454 \times 10^{-6}$ kkg/lb) = 700 kkg from spillage.

Total benzene emissions due to gasoline vending operations: 7,000 kkg.

7.1.3.5 Benzene Emissions Due to Gasoline Combustion

Hydrocarbon emissions from gasoline-powered vehicles without emission controls may be divided into two types: evaporative and exhaust emissions. The evaporative emissions originate from a) the carburetor (evaporation of fuel after a hot engine is turned off); b) the fuel tank (from vents, with emissions increasing as tank temperature increases); and c) the crankcase (from "blowby" past the piston rings). The exhaust emissions result from incomplete combustion of the fuel (PEDCo, 1977).

Benzene emission levels depend not only on benzene levels in gasoline, but also on particular characteristics of the gasoline belend.

For example, if the fuel blend contains ethylbenzene, incomplete combustion may result in the ethylbenzene being converted into benzene; thus, it is possible that more benzene may be exhausted than is present originally in the fuel (PEDCo, 1977). In a material balance scheme, therefore, combustion of fuel in a vehicle engine should be considered both as a use and as a source of benzene. It would be difficult to determine how much of the exhaust benzene is attributable to non-combustion of the benzene originally present in the fuel, and how much is attributable to the breakdown of more complex substances.

Emission control systems in use on current-model motor vehicles include PCV (positive crankcase ventilation), EGR (exhaust gas recirculation), evaporative controls and catalytic oxidation systems (PEDCo, 1977).

Using an estimate of 96 million cars in the United States (PEDCo, 1977), and an emission factor for evaporative emissions of 0.148 g benzene per trip with an average vehicle making 3.3 trips per day (Mara and Lee, 1978), 17,000 kkg of benzene are estimated to be released to the atmosphere through evaporation. It is unknown whether or not control technology was taken into account in the development of the above emission factor.

EPA-ORD and General Motors determined benzene tailpipe emission factors of 0.005 g/mile - 0.020 g/mile for automobiles with catalytic converters, and 0.05 g/mile - 0.15 g/mile for those without catalytic converters (Gray, 1979).

Using an estimate of 96×10^6 vehicles (PEDCo, 1977) (assuming that the number of vehicles hasn't changed substantially since 1976, the year for which the estimate was made), an average of 9,494 miles travelled per car (PEDCo, 1977)(assuming that driving habits haven't changed since 1974, the year for which this estimate was made), an estimate that 73 percent of these vehicles have exhaust controls (PEDCo, 1977) (assuming that this 1976 estimate is still applicable), and the above emission factors, we estimated tailpipe emissions of

benzene to be:

$(96 \times 10^{6}$ vehicles)(9,494 mi/vehicle)(73% emission-controlled)
$(5\text{-}20 \times 10^{-9}$ kkg/mi) = 3,000 - 10,000 kkg.

$(96 \times 10^{6}$ vehicles)(9,494 mi/vehicle)(27% not controlled)
$(5\text{-}15 \times 10^{-8}$ kkg/mi) = 10,000 - 40,000 kkg.

Total benzene exhaust emission: 10,000 - 50,000 kkg.

17,000 kkg + (10,000-50,000 kkg) = 30,000 - 70,000 kkg total benzene emissions attributable to automobile use.

7.1.3.6 Total Benzene Emissions Due to Benzene in Gasoline

Process	Emissions (to air), kkg
Gasoline production	Tabulated in Section 3.1
Gasoline storage	4,000
Gasoline transport	3,000
Gasoline vending	7,000
Gasoline combustion	30,000 - 70,000
SUM:	40,000 - 80,000 kkg

8.0 SUMMARY OF DISPOSAL/DESTRUCTION AS END-PRODUCTS

No data were presented in the readily available literature that permitted evaluation of the disposal of benzene-containing residues or the destruction of benzene-containing end-products. It was judged, however, that benzene would readily volatilize from landfilled solid residues. The question of benzene re-formation during destruction of end-products remains open. A deeper literature search--such as that accompanying a Level II materials balance--would be necessary to obtain information on these points.

9.0 LOCATIONS OF BENZENE EMISSION SITES

Table 9.1 summarizes the relative benzene "activity" at each site containing at least one production or use facility. The "activity" factor is in units of 10^5 kkg benzene produced plus consumed. Since this report assumes throughout that emissions of benzene at a site are proportional to the amount produced or consumed at that site, it is this "activity" factor that is used to rank the sites as "hotspots." The table also shows the number of plants contributing to benzene processes in each area. Also, the locations are grouped by county, so that a group of individual plants in adjacent small towns would not go unremarked.

The results show that the most likely emission sites, in decreasing order, are: Harris County, TX; Jefferson County, TX; Nueces County, TX; Brazoria County, TX; Galveston County, TX; and Puerto Rico.

Table 9.1 Locations of Benzene Emission Sites, 1978

County, State	Number of Plants	"Activity" Factor: Total Production and Consumption in units of 10^5 kkg
Harris Co, TX	9	14
Jefferson Co., TX	9	11
Galveston Co., TX	4	11
Brazoria Co., TX	5	10
Nueces Co., TX	7	9
Puerto Rico	4	9
East Baton Rouge Co., LA	2	5
Iberville Co., LA	1	5
Howard Co., TX	3	3
Los Angeles Co., CA	3	3
Lucas Co., OH	2	3
Caddo Co., LA	2	2
Ector Co., TX	2	2
Tulsa Co., OK	2	2
Gloucester Co., NJ	2	2
Allegheny Co., PA	2	2
Marshall Co., WV	2	2
Saint James Co., LA	1	2
Midland Co., MI	1	2
Baltimore Co., MD	2	2
Virgin Islands	1	1
Boyd Co., KY	1	1
Erie Co., NY	1	1
Calcasieu Co., LA	1	1
Bay Co., MI	1	1
Butler Co., KS	1	1
Philadelphia, PA	1	1
Madison Co., IL	1	1
Delaware Co., PA	1	1
St. Bernard Co., LA	1	1
Cook Co., IL	1	1
Butler Co., OH	1	1
Northampton Co., PA	1	1
Pueblo Co., CO	1	1
Beaver Co., PA	1	1
Somerset Co., NJ	1	1
Jackson Co., MS	1	1
Wetzel Co., WV	1	1
Ascension Co., LA	1	1
Calhoun Co., TX.	1	1
St. Louis Co., MO	1	1
Union Co., NJ	1	1
Middlesex Co., NJ	1	1
Grundy Co., IL	1	1
Contra Costa Co., CA	1	1
Kanawha Co., WV	1	1
Calhoun Co., AL	1	1

10.0 SUMMARY OF UNCERTAINTIES

Table 10.1 summarizes all significant values used in this report and the estimated range or precision for each. As used in the table, N.B. means No Basis for Evaluation.

Table 10.1 Summary of Uncertainties

Section	Description of Value	Value	Estimated Range or Precision
2.0	1978 direct benzene production from petroleum	4,780,000 kkg	± 2%
2.0	1978 direct benzene production from coal	178,000 kkg	± 2%
2.1.2, 2.1.3.1	Total 1975-1979 capacity for benzene production from petroleum	various	± 20%
2.1.2	1975-1979 capacity for benzene production from petroleum for a given plant	various	± 20%
2.1.2	Total 1975-1979 benzene production from petroleum	See Figure 2.1	± 10%
2.1.2	1975-1979 benzene production from petroleum for a given plant	See Figure 2.1	± 30%
2.1.3.1	Total 1978 capacity for benzene production from petroleum through catalytic reformation	3,500,000 kkg	± 20%
2.1.3.1	Total 1978 production of benzene from petroleum through catalytic reformation	2,360,000 kkg	± 30%
2.1.3.2	Benzene emission factor due to production through catalytic reformation	0.01 kkg/kkg	N.B.
2.1.3.2	Benzene emissions due to production through catalytic reformation	20,000 kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.1.4.1	Total 1978 capacity for benzene production from petroleum through toluene dealkylation	1,920,000 kkg	± 20%
2.1.4.1	Total 1978 production of benzene from petroleum through toluene dealkylation	1,300,000 kkg	± 30%
2.1.5.1	Total 1978 capacity for benzene production from petroleum through toluene disproportionation	180,000 kkg	± 20%
2.1.5.1	Total 1978 production of benzene from petroleum through toluene disproportionation	121,000 kkg	± 30%
2.1.6.1	Total 1978 capacity for benzene production from petroleum from pyrolysis gasoline	1,370,000	± 20%
2.1.6.1	Total 1978 production of benzene from petroleum from pyrolysis gasoline	925,000 kkg	± 30%
2.1.7	Benzene emission factor to air due to benzene production from petroleum (all benzene production methods that use petroleum)	1.8×10^{-5} kkg/kkg (See Table 2.1)	low reliability
2.1.7	Benzene emissions to air due to benzene production from petroleum (all benzene production methods that use petroleum)	85 kkg	low reliability
2.1.7	Benzene emission factor to water due to benzene production from petroleum (all benzene methods that use petroleum)	1.3×10^{-4} kkg/kkg (See Table 2.1)	± a factor of 1,000

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.1.7	Benzene emissions to water due to benzene production from petroleum (all benzene production methods that use petroleum)	610 kkg	± a factor of 1,000
2.1.8.1	Benzene emission factors to air due to benzene storage	See Table 2.2	N.B.
2.1.8.1	Benzene emissions to air due to benzene storage	105-4,900 kkg	N.B.
2.1.8.2	Benzene production that was not captively used	2,560,000 kkg	± 30%
2.1.8.2	Benzene emission factors to air due to benzene loading	See Table 2.3	N.B.
2.1.8.2	Benzene emissions to air due to benzene loading	various	N.B.
2.1.8.3	Benzene emission factors to air due to benzene transport	See Table 2.4	N.B.
2.1.8.3	Benzene emissions to air due to transport	various	N.B.
2.1.8.4	Total benzene emissions to air due to transportation, loading, and storage of benzene	2,400-7,200 kkg	N.B.
2.2.1	Total 1975-1979 capacity for benzene production from coal	See Figure 2.2	± 20%
2.2.1	1975-1979 capacity for benzene production from coal for a given plant	See Figure 2.2	± 20%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
2.2.1	Total 1975-1979 benzene from coal	See Figure 2.2	± 10%
2.2.1	1975-1979 benzene production from coal for a given plant	See Figure 2.2	± 30%
3.1	Benzene emission factors to air due to indirect production of benzene from petroleum refineries	See Table 3.1	N.B.
3.1	Benzene emissions to air due to indirect production of benzene from petroleum refineries operating at 1977 capacity	20,000 kkg	N.B.
3.1	Benzene emission factor to water due to indirect production of benzene from petroleum refineries	$1.64 \times 10^{-10} \frac{\text{kkg}}{\text{bbl}}$	± a factor of 10
3.1	Total 1978 benzene emissions to water due to indirect production of benzene from petroleum	1 kkg	± a factor of 10
3.1	1978 benzene emissions by state to water due to indirect production of benzene from petroleum refineries	See Figure 3.1	± a factor of 10
3.2	Annual coal consumption capacity of coke producing plants	88,000,000 kkg	± 20%
3.2	Walker's (1976) benzene emission factor to air due to coke oven operations	$9.80 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg coke produced}}$	± a factor of 6

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
3.2	Total benzene emissions, based on Walker's (1976) emission factor, to air due to coke oven operations	59,200 kkg	± a factor of 6
3.2	PEDCo's (1977) benzene emission factor to air due to coke oven operations	$7.8 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	± a factor of 10
3.2	Total benzene emissions based on PEDCo's (1977) emission factor due to coke oven operations	6,600 kkg	± a factor of 10
3.2	Mara and Lee's (1978) benzene emission factor to air due to coke oven operations	$3 \times 10^{-5} \frac{\text{kkg benzene}}{\text{kkg coal used}}$	N.B.
3.2	Total benzene emissions based on Mara and Lee's (1978) emission factor due to coke oven operations	3,000 kkg	N.B.
3.2	Benzene emissions by state based on Mara and Lee's (1978) emission factor due to coke oven operations	See Figure 3.2	N.B.
3.3	Annual oil discharge to oceans according to Walker (1976)	$11\text{-}12 \times 10^{9}$ lbs/year	N.B.
3.3	Benzene content of oils	0.001 - 0.4%	± a factor of 400
3.3	Annual benzene discharge to oceans according to Walker (1976)	$10\text{-}11 \times 10^{3}$ kkg	± a factor of ≥400

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
3.3	Annual oil discharge to U.S. waters according to Versar (1977)	4,990,691 gal	N.B.
3.3	Annual benzene discharge to U.S. waters according to Versar (1977)	30 kkg	± a factor of ≥400
3.4	Gross annual discharge of benzene to water from various indirect sources	various	N.B.
4.1	1975-1979 benzene imports	See Table 4.1	± 20%
4.2	Benzene emission factor for marine loading during importation	$2.0 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg unloaded}}$	± a factor of 10
4.2	Benzene emission factor for transport of imported benzene	$1 \times 10^{-4} \frac{\text{kkg benzene}}{\text{kkg transported/wk}}$	± a factor of 10
4.2	Total 1978 benzene emissions due to benzene imports	25 kkg	± a factor of 10
4.2.1	1978 benzene emissions to air due to benzene imports	13 kkg	± a factor of 15
4.2.2	1978 benzene emissions to water due to benzene imports	13 kkg	± a factor of 15
5.1	Total 1978 consumptive use of benzene	5,389,000 kkg	± 20%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5.2	1975-1979 consumption of benzene for derivative synthesis	See Table 5.2	± 20%
5.2	1978 production of each benzene derivative	See Table 5.1	± 10%
5	Capacities for production of each benzene derivative	various	± 20%
5	Production of each benzene derivative by a given plant	various	± 30%
5	Consumption of benzene for the synthesis of each benzene derivative (except anthraquinone and biphenyl) by a given plant	various	± 40%
5.3.8.2	Benzene consumption for anthraquinone synthesis	23,000 kkg	N.B.
5.3.9.3	Benzene consumption for biphenyl synthesis	11,000 kkg	± 50%
5.3.1.3.1	Benzene emission factors to air and corresponding 1978 emissions due to ethylbenzene synthesis	See Table 5.3	N.B.
5.3.1.3.2	Benzene emission factor to water due to ethylbenzene synthesis	1.9×10^{-4} kkg/kkg	± a factor of 5
5.3.1.3.2	1978 benzene emissions to water due to ethylbenzene synthesis	720 kkg	± a factor of 10

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5.3.2.3	Benzene emission factor due to cumene synthesis	0.25×10^{-3} kkg/kkg	N.B.
5.3.2.3	1978 benzene emissions to air due to cumene synthesis	380 kkg	N.B.
5.3.3.3	Benzene emission factor due to cyclohexane synthesis	2.8×10^{-3} kkg/kkg	± a factor of 10
5.3.3.3.1	Benzene emissions to air due to cyclohexane synthesis	3,000 kkg	± a factor of 10
5.3.3.3.2	Benzene emissions to water due to cyclohexane synthesis	30 kkg	± a factor of 10
5.3.4.3.1	Benzene emission factor to air due to maleic anhydride synthesis	0.20 kkg/kkg	+10%, -90%
5.3.4.3.1	1978 benzene emissions to air due to maleic anhydride synthesis	34,000 kkg	+10%, -90%
5.3.4.3.2	1976 benzene emissions to water due to maleic anhydride synthesis	8 kkg	N.B.
5.3.5.3.1	Benzene emission factors and corresponding 1978 benzene emissions to air due to nitrobenzene synthesis	See Table 5.3	N.B.
5.3.6.2.1	Benzene emission factors to air due to chlorobenzene synthesis	See Table 5.6	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
5.3.6.2.1	1978, 1979 benzene emissions to air due to chlorobenzenes synthesis	See Table 5.7	N.B.
5.3.7.3	Benzene emission factor to air due to alkylbenzene synthesis	5×10^{-4} kkg/kkg	N.B.
5.3.7.3.1	1978 benzene emissions to air due to alkylbenzene synthesis	170 kkg	N.B.
5.3.9.3	Benzene emission factor due to biphenyl synthesis	5.9×10^{-3} kkg benzene emitted per kkg benzene consumed	± a factor of 2
5.3.9.3.1	1978 benzene emissions to air due to biphenyl synthesis	64 kkg	± a factor of 3
5.3.9.3.2	1978 benzene emissions to water due to biphenyl synthesis	0.3 kkg	± a factor of 3
6.1	Total 1978 nonconsumptive use of benzene	270,000 kkg	± 60%
6.3.1.2	1978 solvent nonconsumptive use of benzene according to Neufeld et al. (1978)	9,500 kkg	+10%, -50%
6.3.1.2	1978 solvent nonconsumptive use of benzene according to Mara and Lee (1978)	27,000 kkg	± 80%

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
6.3.1.3	1978 benzene emissions due to solvent non-consumptive use of benzene	2,900 kkg	N.B.
6.3.1.3.1	1978 benzene emissions to air due to solvent nonconsumptive use of benzene	1,450 kkg	N.B.
6.3.1.3.2	1978 benzene emissions to water due to solvent nonconsumptive use of benzene	1,450 kkg	N.B.
7.1.1	Volume percent benzene in gasoline, 1979	2% ($^{v}/v$)	$\pm$ 50%
7.1.2	1979 Annual Domestic Gasoline Consumption (ADGC)	1.08×10^{11} gal	$\pm$ 10%
7.1.2	Amount of benzene in gasoline, 1979	2×10^{9} gal; 7×10^{6} kkg	$\pm$ 60%
7.1.3.2	Capacity of floating-roof storage tanks	2.3×10^{6} gal	N.B.
7.1.3.2	Average tank retention time	30 days	N.B.
7.1.3.2	Average percent of tank filled	75%	N.B.
7.1.3.2	Emission factor for hydrocarbon standing storage losses	132 lb/day/tank	N.B.
7.1.3.2	Emission factor for hydrocarbon withdrawal losses	0.025 lb/10^{3} gal	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.2	Conversion factor, benzene liquid volume to benzene vapor weight	0.45	± 5%
7.1.3.2	Emissions of benzene to air during standing storage, 1979	1,000 kkg	N.B.
7.1.3.2	Emissions of benzene to air during withdrawal, 1979	10 kkg	N.B.
7.1.3.2	Daily volume of gasoline handled by bulk plants	4,000 gal	± 25 %
7.1.3.2	Number of bulk plants, 1979	20,000	± 20%
7.1.3.2	Annual volume of gasoline handled by bulk plants	3×10^{10} gal	± 50 %
7.1.3.2	Emissions of benzene to air due to tank breathing, 1979	500 kkg	N.B.
7.1.3.2	Percent above-ground fixed-roof tanks at bulk plants	70%	± 10%
7.1.3.2	Annual volume stored in above-ground fixed-roof tanks	2×10^{10} gal	± 60%
7.1.3.2	Emissions of benzene to air from filling above-ground fixed-roof tanks	1,600 kkg	± a factor of 4

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.2	Emissions of benzene from filling underground tanks	1,000 kkg	± a factor of 4
7.1.3.2	Emissions of benzene due to all gasoline storage	4,000 kkg	minimum: does not consider all possible losses
7.1.3.3	Emission factor for hydrocarbon losses during tank car/truck splash loading	12 lb/10^3 gal	N.B.
7.1.3.3	Emission factor for hydrocarbon losses during tank car/truck submerged loading	5 lb/10^3 gal	N.B.
7.1.3.3	Emission factor for hydrocarbon losses during marine loading	1.8 lb/10^3 gal	N.B.
7.1.3.3	Emission factor for hydrocarbon losses during transit	3 lb/wk/10^3 gal	N.B.
7.1.3.3	Emission factor for hydrocarbon losses during unloading	2.1 lb/10^3 gal	N.B.
7.1.3.3	Emissions of benzene to air due to transport of gasoline	3,000 kkg	N.B.
7.1.3.4	Hydrocarbon emission rate, filling storage tank - submerged	7.3 lb/10^3 gal	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.4	Frequency of use: filling storage tank - submerged	50%	N.B.
7.1.3.4	Hydrocarbon emission rate, filling storage tank - splash	11.5 $lb/10^3$ gal	N.B.
7.1.3.4	Frequency of use: filling storage tank - splash	25%	N.B.
7.1.3.4	Hydrocarbon emission rate, filling storage tank - balanced	0.3 $lb/10^3$ gal	N.B.
7.1.3.4	Frequency of use: filling storage tank - balanced	25%	N.B.
7.1.3.4	Hydrocarbon emission rate, underground task breathing	1 $lb/10^3$ gal	N.B.
7.1.3.4	Frequency of use: underground task breathing	100%	N.B.
7.1.3.4	Hydrocarbon emission rate, uncontrolled vehicle refueling	9.0 $lb/10^3$ gal	N.B.
7.1.3.4	Frequency of use: uncontrolled vehicle refueling	75%	N.B.
7.1.3.4	Hydrocarbon emission rate, controlled vehicle refueling	0.9 $lb/10^3$ gal	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.4	Frequency of use: controlled vehicle refueling	25%	N.B.
7.1.3.4	Hydrocarbon emission rate, spillage	0.7 lb/10^3 gal	N.B.
7.1.3.4	Frequency of use, spillage	100%	No range
7.1.3.4	Benzene emissions, filling storage tanks - submerged	2,000 kkg	N.B.
7.1.3.4	Benzene emissions, filling storage tanks - splash	1,000 kkg	N.B.
7.1.3.4	Benzene emissions, filling storage tanks - balanced	30 kkg	N.B.
7.1.3.4	Total filling emissions	3,000 kkg	N.B.
7.1.3.4	Benzene emissions, underground task breathing	400 kkg	N.B.
7.1.3.4	Benzene emissions, uncontrolled vehicle refueling losses	3,000 kkg	N.B.
7.1.3.4	Benzene emissions, controlled vehicle refueling losses.	100 kkg	N.B.
7.1.3.4	Total vehicle refueling benzene emissions	3,000 kkg	N.B.
7.1.3.4	Spillage benzene emissions	700 kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.4	Total benzene emissions, gasoline vending operations	7,000 kkg	N.B.
7.1.3.5	Estimate of vehicles in U.S.	96 million	N.B.
7.1.3.5	Benzene emission factor for evaporative emissions	0.148 g/trip	N.B.
7.1.3.5	Average number of trips per vehicle per day	3.3 trips/day	N.B.
7.1.3.5	Benzene emissions due to evaporation	17,000 kkg	N.B.
7.1.3.5	Benzene tailpipe emission factors - non-catalytic	0.05 - 0.15 g/mile	N.B.
7.1.3.5	Benzene tailpipe emission factors - catalytic	0.005 - 0.020 g/mile	N.B.
7.1.3.5	Average number of miles driven per car	9,494 miles	N.B.
7.1.3.5	Percent of vehicles with exhaust controls	73%	N.B.
7.1.3.5	Benzene exhaust emissions, controlled	3,000 - 10,000 kkg	N.B.
7.1.3.5	Benzene exhaust emissions, uncontrolled	10,000 - 40,000 kkg	N.B.
7.1.3.5	Total benzene exhaust emissions	10,000 - 50,000 kkg	N.B.
7.1.3.5	Total benzene emissions, auto use	30,000 - 70,000 kkg	N.B.

Table 10.1 Summary of Uncertainties (continued)

Section	Description of Value	Value	Estimated Range or Precision
7.1.3.6	Sum of benzene emissions due to benzene in gasoline	40,000 - 80,000 kkg	N.B.

11.0 DATA GAPS AND RECOMMENDATIONS

In the course of performing this Level I materials balance, the following significant data gaps were encountered:

11.1 EMISSIONS DUE TO BENZENE PRODUCTION BY COKE OVEN PLANTS

Light oil containing benzene is produced as a byproduct of coal coking. In Section 3.2, a question arose concerning the fate of 472,000 kkg of benzene-containing light oil produced by coke ovens. This amount was the difference between the light oil production capacities of non-benzene-producing plants (798,000 kkg) and the amount of light oil accounted for by sales to other plants for benzene extraction (326,000 kkg). A more detailed literature search and inquiries to the appropriate companies should be made to determine what fraction of this unaccounted-for light oil is a source of benzene emissions.

This problem is one aspect of the larger question of benzene emissions due to coal coking. The readily available literature did not distinguish between benzene-producing and non-benzene-producing coking operations. A Level II survey of primary literature and, if necessary, monitoring to determine relative emissions for the two types of coking plants should be performed.

11.2 BREAKDOWN OF EMISSIONS DUE TO PETROLEUM REFINING BY METHOD

No data were available to distinguish, for instance, between emissions due to catalytic reformation and those due to toluene dealkylation. The emission factors for these processes may be quite different. A more detailed literature search would reveal whether or not monitoring would be necessary. If monitoring were recommended, it might be satisfactory to determine an emission factor for one process plus relative emission concentrations for the other three. This would permit estimation of emission factors for the latter three.

11.3 BENZENE EMISSIONS TO WATER

In the absence of data, it is generally assumed (as it was in this report) that the majority of benzene emissions were to the air. A closer search for wastewater monitoring data from benzene producing and consuming plants (including coke ovens) should be performed. If no data exist, waste stream volumes should be ascertained from industry and maximum benzene emissions should be calculated from the solubility limit (0.7 g/l). This would give an estimate of the relative importance of water emissions. Monitoring resources could be allocated accordingly.

11.4 TREATMENT OF SOLID RESIDUES

Data on production and treatment of benzene-containing solid residues (tars, gums, sludges) were unavailable for the Level I study. Industry sources should be interviewed for information on both refinery solids and solid residues formed during consumptive use. Information on rates of solid generation, compositions of residues, and disposal methods and efficiencies should be sought.

11.5 EMISSIONS DUE TO MINOR CONSUMPTIVE USES

Neither process information nor emission factors were available for the minor consumptive uses of benzene: anthraquinone and biphenyl. These data are probably available in the literature (perhaps dye industry or PCB information), and it should be obtained in order to form a more complete materials balance.

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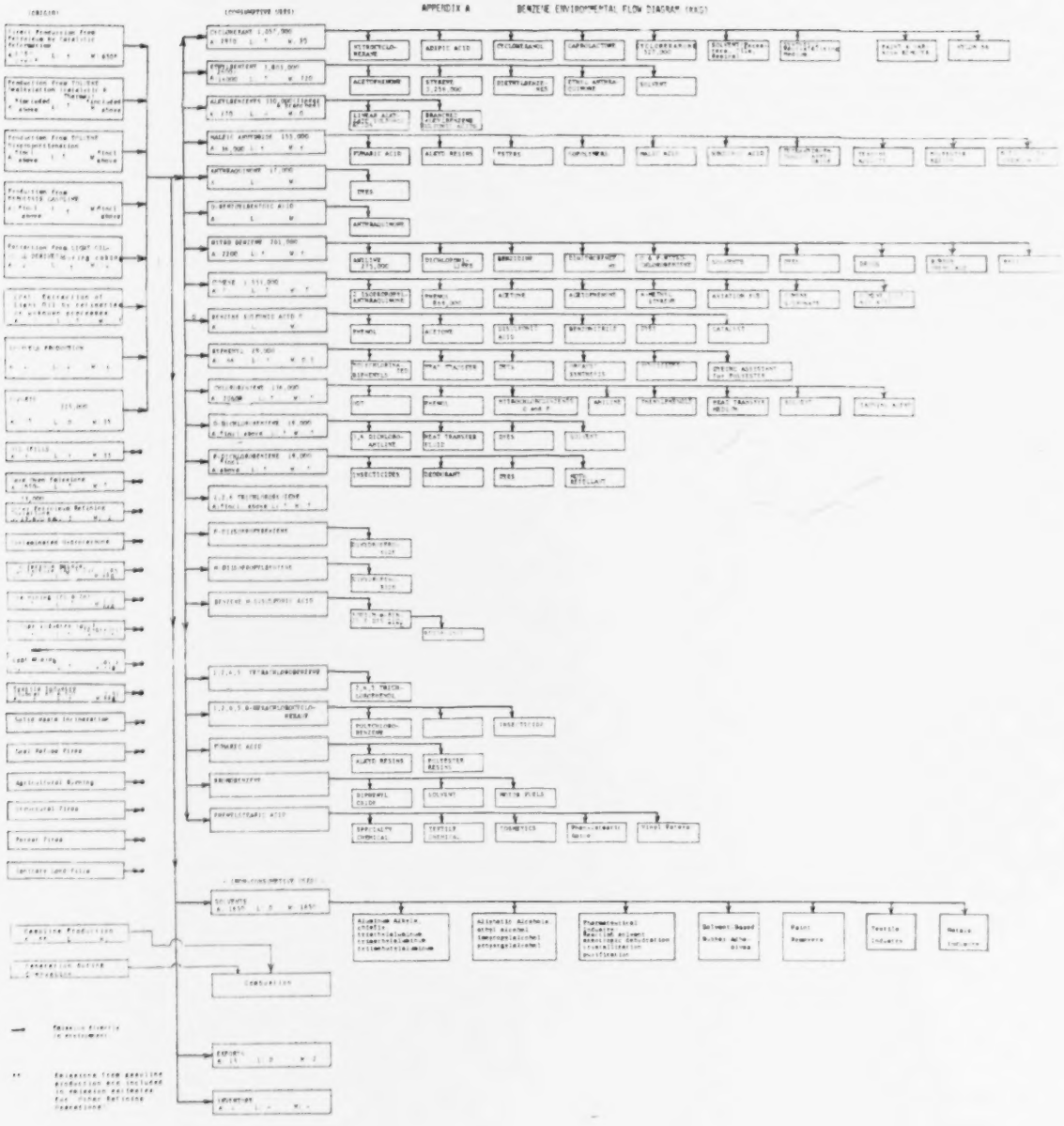
APPENDIX A

ENVIRONMENTAL FLOW DIAGRAM FOR BENZENE


APPENDIX A
BENZENE ENVIRONMENTAL FLOW DIAGRAM (1982)

APPENDIX B

PROCESS FLOW DIAGRAMS FOR PRODUCTION OF BENZENE FROM PETROLEUM

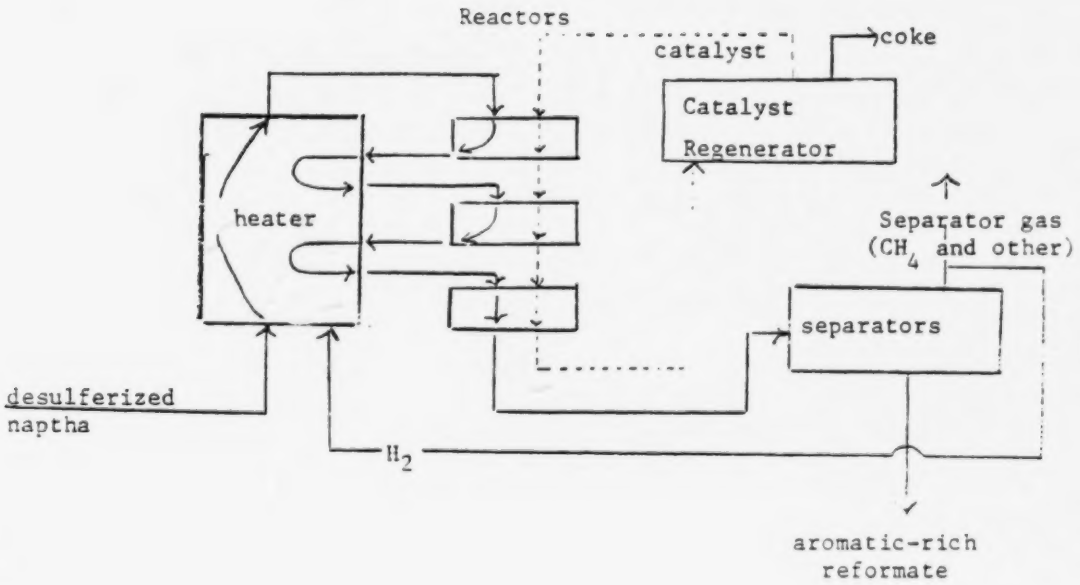


Figure B-1 Platforming Method of Catalytic Reformation (Kirk-Othmer, 1976)

Desulfurized naphtha is mixed with recycled hydrogen, heated, then fed through a series of moving catalyst bed reactors with intermediate heating. The platinum chloride-rhenium chloride catalyst is regenerated by controlled combustion coke removal, and is recycled. The reformate from the reactors passes through the separator where hydrogen and other gases are removed. The aromatic-rich reformate then goes to a stabilizer. Aromatics are extracted from the stabilized reformate.

An example of the separation process is the Sulfolane process which is presented schematically in Figure B-2 on the next page. An aliphatic-aromatic stream is charged to the extractor through which the solvent is flowing in a counter-current. The solvent will dissolve the hydrocarbons and carry them to the extractive stripper where most of the hydrocarbons are separated from the solvent. The hydrocarbons are recycled through this system again, then are issued to the extract recovery column where additional solvent contamination is removed. The resulting BTX stream is then fractionated into individual products.

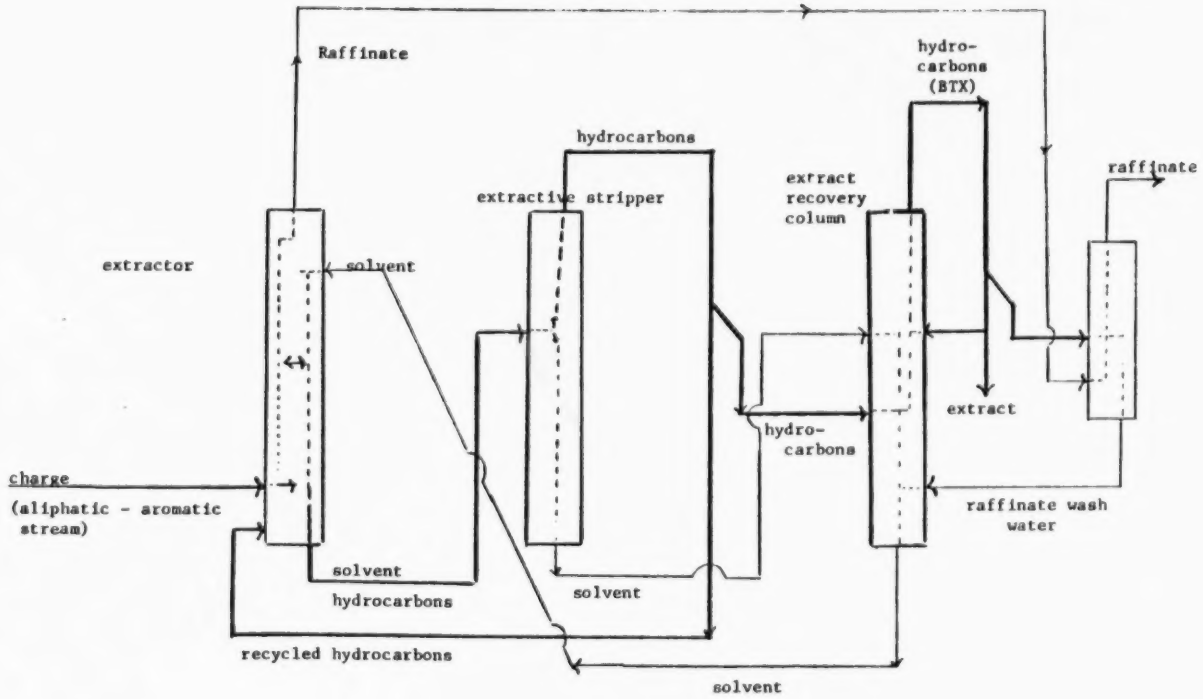


Figure B-2 Separation of Benzene from Catalytic Reformate by the Sulfolane Process (Kirk-Othmer, 1976)

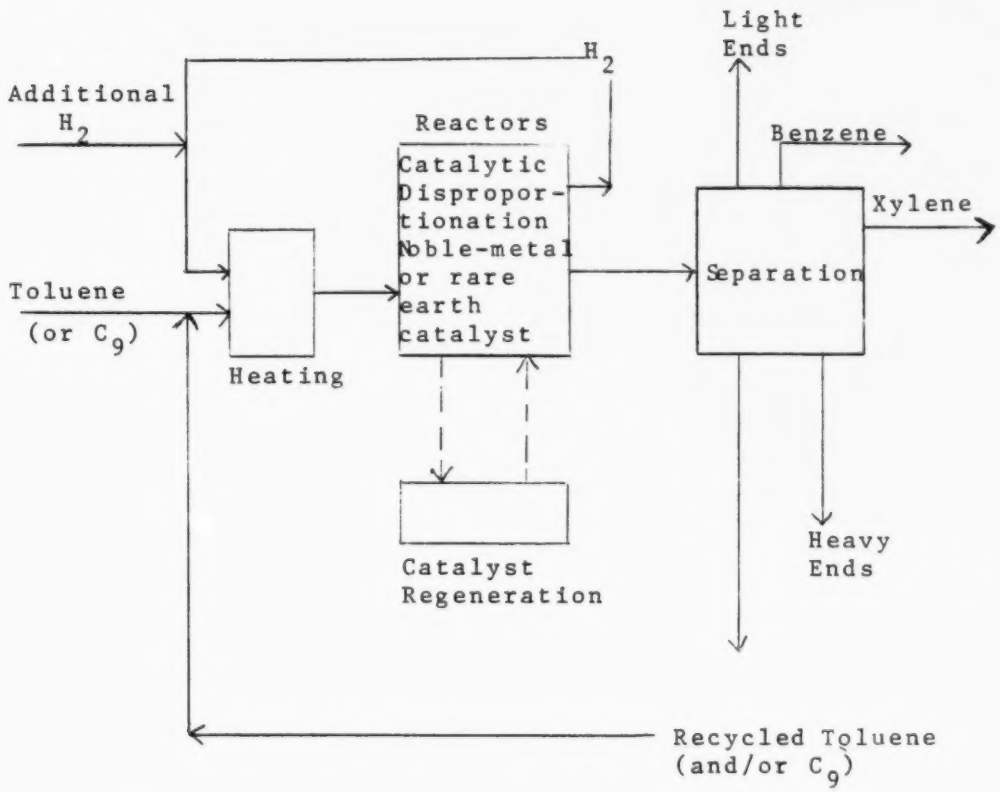


Figure B-3 Toluene Disproportionation by the Tatoray Process
(adaptation from Kirk-Othmer, 1976)

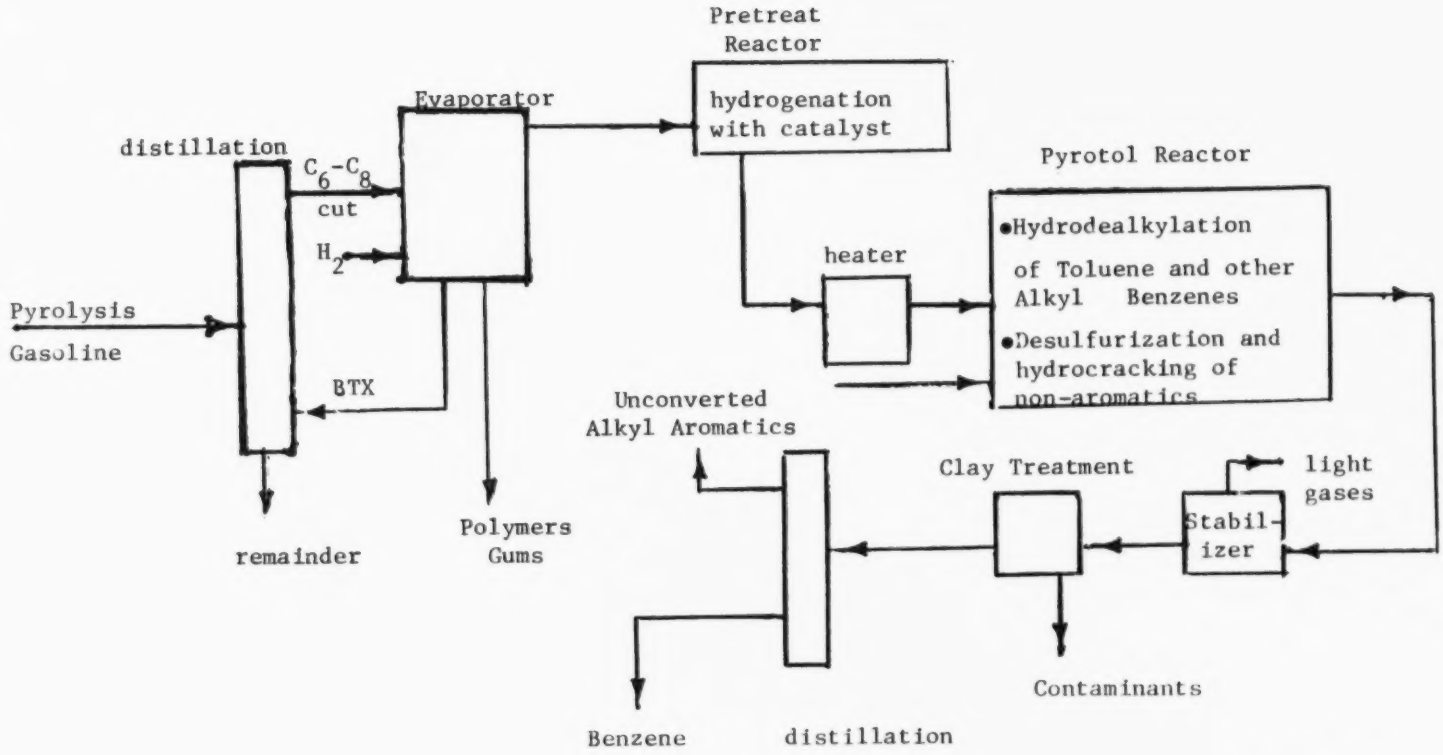


Figure B-4 Recovery of Benzene from Pyrolysis Gasoline by the Pyrotol Process (Kirk-Othmer, 1976)

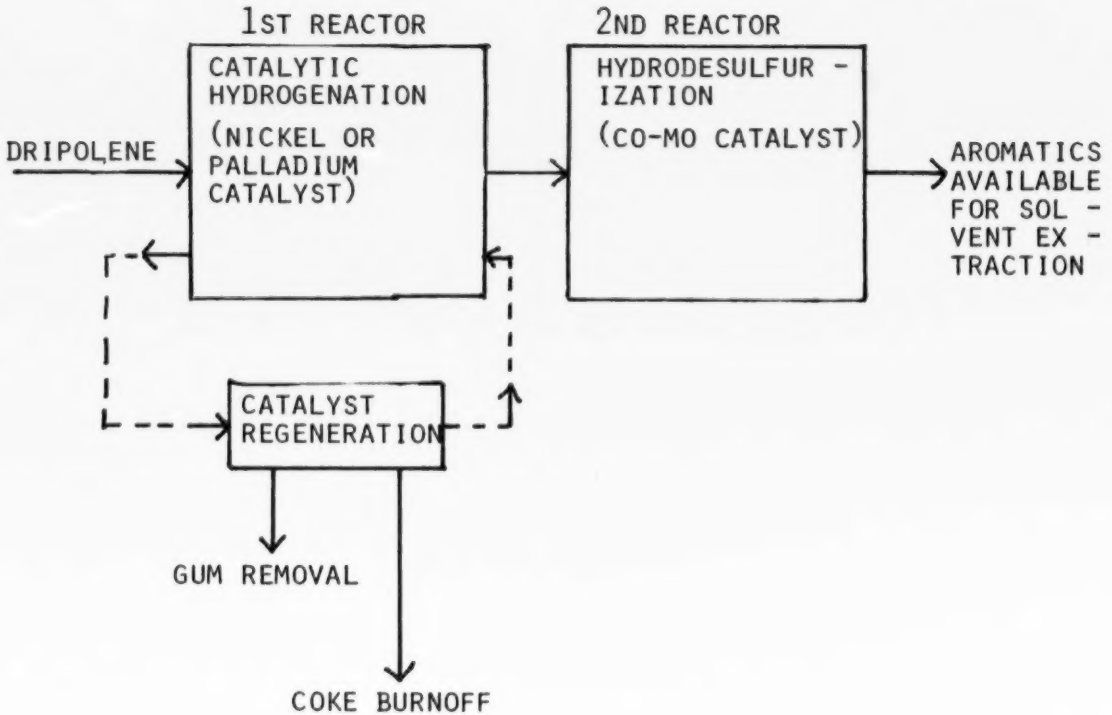


Figure B-5 Recovery of Benzene from Pyrolysis Gasoline (Dripolene) by the IFP (Institute Francaise de Petrole) Process: After Kirk-Othmer, 1976